Science
Library

126

AUG 15 1938

Volume 46 August, 1938 Number 2

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

Studies on the Behavior of Manganese in Soils. A. L. PRINCE AND S. J. TOTH 83
The Movement of Water in Heavy Soils after Irrigation. E. C. CHILDS. 95
A Field Outfit for Determining the Moisture Content of Soils. GEORGE JOHN BOUYOUCOS 107
Hydrogen-ion Activity of Colloidal Acids in Soils. AMAR NATH PURI AND A. N. DUA 113
On the Formation of Structure in Soil: IV. The Structure of Mixed Clay-sand and Clay-humus Formations. D. I. SIDERI 129
Microbial Activities in Soil: V. Microbial Activity and Organic Matter Transformation in Palouse and Helmer Soils. S. C. VANDECAVEYE AND H. KATZNELSON 139
Book Reviews 169

Published Monthly by THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES, BALTIMORE, MARYLAND, U. S. A.

Copyright, 1938, The Williams & Wilkins Company

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

A. W. Blair, J. S. Joffe, L. L. Lee, H. C. McLean, A. L. Prince, J. W. Shive, H. B. Sprague, R. L. Starkey, and S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

F. J. ALWAY
University of Minnesota, St. Paul, Minn.

K. ASO
Imperial University, Tokyo, Japan

C. BARTHEL
Lantbrukshögskolan, Uppsala, Sweden

RICHARD BRADFIELD
College of Agriculture, Cornell University, Ithaca, New York

B. C. BURT
Imperial Council of Agricultural Research, New Delhi, India

H. J. CONN
New York State Experiment Station, Geneva, N. Y.

ALBERT DEMOLON
Ministry of Agriculture, Paris, France

E. B. FRED
University of Wisconsin, Madison, Wis.

V. V. GEMMERLING
Agronomitsheskii Institute, Moskovskii Universitat, Moscow, U. S. S. R.

J. E. GREAVES
Utah Agricultural College, Logan, Utah

D. J. HISSINK
Soil Science Institute, Groningen, Holland

D. R. HOAGLAND
University of California, Berkeley, California

O. LEMMERMANN
Berlin-Zehlendorf, Germany

C. B. LIPMAN
University of California, Berkeley, Calif.

BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

HENRIK LUNDEGÅRDH
Centralanstalten för jordbruksförsök, Stockholm, Sweden

M. M. MCCOOL
Boyce-Thompson Institute, Yonkers, N. Y.

W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

S. MATTSON
Lantbrukshögskolan, Uppsala, Sweden

S. MIKLASEWSKI
Institute of Soil Science, Warsaw, Poland

E. A. MITSCHERLICH
University of Königsberg, Germany

C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

D. N. PRIANISHNIKOV
Timiryazev Academy, Moscow, U. S. S. R.

THEO. REMY
Bonn-Rhein, Germany

G. W. ROBINSON
University College of Wales, Bangor, Great Britain

G. ROSSI
R. Università di Napoli, Portici, Italy

E. J. RUSSELL
Rothamsted Experimental Station, Harpenden England

O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.

ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.

EMILE H. DEL VILLAR
Forestry Institute, Madrid, Spain

S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter, May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.
Subscription price $5.00 per volume. Single numbers, $1.00.

STUDIES ON THE BEHAVIOR OF MANGANESE IN SOILS[1]

A. L. PRINCE AND S. J. TOTH

New Jersey Agricultural Experiment Station

Received for publication January 27, 1938

Numerous studies (4, 6, 7) on the rôle and behavior of manganese in soils are presented in the literature. Some of the conditions affecting the solubility of manganese in the soil solution, such as pH and oxidizing-reducing states, have been rather clearly elucidated by various investigators (4, 6). The effect of liming and other fertilizer treatments on exchangeable manganese has been brought out in the work of Schollenberger and Dreibelbis (17), Mann (7), Willis (20), and Connor (4). Robinson (14) has pointed out that manganese may occur in soils largely as manganese dioxide concretions concentrated in the sand and silt fractions. On the other hand, he has shown that the bulk of the exchangeable manganese is located in the colloidal fraction. Gilligan (5) has pointed out that the electrodialyzable manganese content of limed soils is higher than that of unlimed soils.

The purpose of the present investigation was to study some of the factors governing the behavior of manganese in soils under definite treatment when subjected to salt extraction and electrodialysis, with the hope that the results would be helpful in the solution of soil and crop problems involving the use of manganese. All the soils studied, with the exception of Penn silt loam, were of Coastal Plain origin. For a study of the delivery rates of manganese during electrodialysis, cultivated soils from the following localities were used:

Sassafras sandy loam: 0″–6″ depth, obtained from the Kilbourne Farm at the New Jersey Agricultural Experiment Station, New Brunswick, N. J.

Sassafras sand: 0″–6″ depth, obtained near Hammonton, N. J.

Collington loam: 0″–6″ depth, obtained outside Matawan, N. J. This field had been recently limed.

Colts Neck loam: 0″–6″ depth, obtained near Colts Neck, N. J.

In addition to the studies on these soils further studies were carried out with certain soils which were later partially saturated with manganese. These samples consisted of the B horizon from the following two profiles:

Sassafras loam: obtained near Colonial Gardens, New Brunswick, N. J.

Penn silt loam: obtained from a road cut about 2 miles from Franklin Park on the road to Griggstown, N. J.

---

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

Certain limed and unlimed plot soils at the New Jersey Experiment Station were also investigated in connection with this problem. The soil on these plots was Sassafras loam and had received varying amounts of calcium limestone and dolimitic limestone at 5-year intervals for the last 25 years.

METHODS

The soils that were partially saturated with manganese were prepared by leaching 500 gm. of the soil with 10 liters of a normal solution of $MnCl_2$ on a Büchner funnel using gentle suction. The soils were then washed with distilled water until free from chlorides, air-dried, and passed through a 2-mm. sieve.

Electrodialysis, cation exchange capacity, and ultimate pH determinations of the soil samples were carried out as reported elsewhere (12). Of the partially saturated manganese soils, however, a 25-gm. sample was used instead of the usual 100-gm. sample, and the period of electrodialysis was 38 hours.

Exchangeable manganese was obtained both by the normal ammonium acetate and 0.05*N* HCl methods.

Total manganese in the soils was determined by fusing with potassium bisulfate followed by the usual colorimetric periodate method (1, p. 8, par. 24).

In the extracts and certain dialyzates, interfering salts and organic matter were removed prior to the determination of manganese by the periodate method.

The manganese in the cathode dialyzates from the soils containing adsorbed manganese was determined gravimetrically by filtering off the hydrated manganese micelles and igniting to Mn_3O_4. Silica was removed by the addition of a few drops of hydrofluoric acid to the precipitate, followed by ignition to constant weight. In the case of the manganese soils that were treated with $Ca(OH)_2$, it was necessary to remove calcium prior to igniting the hydrated manganese oxides. This was accomplished by leaching the filtered micelles from the cathode dialyzates with normal ammonium chloride solution until free from calcium.

SOME GENERAL OBSERVATIONS ON THE BEHAVIOR OF $MnCl_2$ AND ADSORBED MANGANESE IN SOILS UNDER ELECTRODIALYSIS

During the electrodialysis of a $MnCl_2$ solution certain observations of importance were noted. Coincident with the passage of the electric current through the cell, a light brown floc of $Mn(OH)_2$ appeared in the cathode chamber. The pH in this compartment after 15 minutes of electrodialysis was between 9.0 and 9.2. Continuing the electrodialysis for a period of 1 hour brought the pH value of the catholyte to about 9.2–9.4. This pH range no doubt expresses the basicity of $Mn(OH)_2$. The same observations were noted when soils containing adsorbed manganese were electrodialyzed. The precipitation of $Mn(OH)_2$ from solutions of manganese chloride begins at pH 8.4, according to Britton (3, p. 301), and does not reach completion until the pH is between 9

and 10. Schollenberger (15) observed that the addition of precipitated $Mn(OH)_2$ to soil had the same effect of increasing the pH in the suspensions as did equivalent $Ca(OH)_2$ up to pH 7.5, but further additions of $Mn(OH)_2$ did not result in higher pH values. Some later observations by the same author (16) suggest that this may have been because the manganese adsorbed by the soil above a certain level tended to become oxidized to forms inactive as base by exposure to the air.

Certain difficulties were encountered in determining the manganese electrodialyzed from partially saturated manganese soils. When the determinations were based solely on the amount of manganese transported and precipitated in the cathode chamber, the results were always low. The low values were not due to the presence of large quantities of soluble manganese in the clear catholyte filtrate, but rather to a failure to determine the manganese which had precipitated in the parchment paper facing the cathode. In order to illustrate how the electrodialyzed manganese was distributed in various parts of the cell, the following data are given on the electrodialysis of Penn silt loam:

Electrodialysis of Penn silt loam containing adsorbed manganese

Total Mn by electrodialysis	10.23	m.e. per 100 gm. soil
Precipitated Mn micelles in catholyte	9.94	" " " " "
Precipitated Mn in the parchment paper	0.28	" " " " "
Soluble Mn in catholyte filtrate	0.01	" " " " "

In the electrodialysis of manganese soils that were treated with $Ca(OH)_2$, greater quantities of Mn were found in the parchment paper (0.9–1.4 m.e.) than the values recorded above. In the electrodialysis of soils, basoids and acidoids are also transported to the cathode (9, 18), and these would be weighed along with the Mn_3O_4 precipitate. Silica was removed from the precipitate, however, by the addition of a few drops of hydrofluoric acid (loss in weight of precipitate from 100 gm. of soil was about 5–15 mgm.), and since only small quantities (0.5–3.0 mgm.) of R_2O_3 are transported to the cathode (9, 12, 18), the effect of this transport would not seriously increase the values for the electrodialyzable manganese.

A study was also made of the behavior of Mn $(OH)_2$ floc during electrodialysis. For this purpse 20 m.e. of $MnCl_2$ and 20 m.e. of NaOH were added to the center compartment of a standard Mattson cell. For comparative purposes a similar procedure was followed for an $Fe(OH)_3$ sol. The precipitates were allowed to stand over night in the cells, and the following day the cells were placed in the circuit, and the flocs were electrodialyzed free from soluble ions. The following qualitative observations were noted:

A considerable quantity of both the manganese and iron hydroxide flocs were transported to the cathode, but the quantity of $Mn(OH)_2$ floc exceeded that of the $Fe(OH)_3$.

As the quantity of soluble ions diminished, the transport of both flocs decreased.

The transport of the $Mn(OH)_2$ to the cathode continued in appreciable quantities even after the floc was free from soluble ions, whereas only traces of the $Fe(OH)_3$ floc migrated under these conditions.

The color of the transported $Mn(OH)_2$ micelles underwent a transition from a very light brown to a very dark brown during electrodialysis, indicating a possible change in the nature of the floc. This change in color of the floc is probably due to oxidation. It is possible that the course of the reaction and the color change are as follows: $Mn(OH)_2$ (white) $\rightarrow$ MnO_2 (dark brown).

These observations, although qualitative in character, are important in the elucidation of the effect of lime on the transport of manganese from soils during electrodialysis, which will be discussed later.

It would be expected that the solubility of air-dry $Mn(OH)_2$ would be greater in 0.05 *N* HCl than in neutral normal ammonium acetate. An air-dried precipitate of $Mn(OH)_2$ was leached to 250 cc. with the extractants. The weight of the residue after this treatment was 0.0289 gm. by the 0.05 *N* HCl method and 0.0654 gm. by the normal ammonium acetate method. It is possible that oxidation and drying may affect the solubility of the floc, but in this study only relative solubilities are concerned.

RELEASE OF MANGANESE FROM SOME COASTAL PLAIN SOILS BY ELECTRODIALYSIS

The release of manganese from some soil colloids by electrodialysis has been studied by Mattson (8). In some respects the behavior of this cation is similar

TABLE 1

Some data on Coastal Plain soils with respect to total and exchangeable manganese contents

Mn expressed in m.e. per 100 gm. soil

SOIL TYPE	FIELD pH	ULTIMATE pH	TOTAL Mn	EXCHANGEABLE Mn BY *N* NH_4Ac	EXCHANGEABLE Mn BY ELECTRODIALYSIS	TOTAL ELECTRODIALYZABLE Mn
Sassafras loam	5.20	4.23	0.761	0.007	0.008	0.034
Sassafras sand	6.35	4.18	0.226	0.007	0.006	0.013
Collington sandy loam	5.77	3.67	0.423	0.007	0.005	0.032
Colts Neck loam	4.83	4.15	1.155	0.029	0.026	0.098

to that of magnesium, iron, and aluminum, namely, that more of this cation is released in the later periods of electrodialysis than in the earlier stages. Four Coastal Plain soils were studied for this purpose. Before the delivery rates of manganese are discussed, some other important data on these soils are presented in table 1. The total manganese content as given in column 3 shows a variation from 0.226 m.e. per 100 gm. for Sassafras sand to 1.155 m.e. for Colts Neck loam. Exchangeable manganese by the normal ammonium acetate method on these soils was very low, ranging from 0.007 m.e. to 0.029 m.e. per 100 gm. soil. A good agreement between the exchangeable manganese by electrodialysis and by salt extraction may be noted in this table. The exchangeable manganese by electrodialysis may be defined as that manganese existing in the catholyte before the appearance of a large volume of sediment. This usually consists of the manganese appearing in the catholyte during the

0–8-hour period of electrodialysis. The manganese in this fraction exists primarily as soluble ions at pH values above 8.2. This fact is in line with McCool's findings that soluble manganese does exist in solutions of high pH values (6). The total electrodialyzable manganese represents the sum of the soluble manganese and the manganese transported as ionogenic complexes. It may be observed from the table that these values far exceed the exchangeable values.

Table 2 shows the delivery rates of manganese during electrodialysis from these four soils. Certain general conclusions may be drawn from these data. Simultaneously with the decrease in titrable bases, ionization and transport of manganese to the cathode increases to a maximum and then decreases. This maximum depends on the original base saturation of the soil, and with the soils studied it generally occurs between the 8–12- or the 12–16-hour periods of electrodialysis. The decrease after the maximum is reached is due, as pointed out previously (9, 12), to the formation of a sediment on the inner face of the cathode parchment paper. The factors influencing migration rates of the ionized complexes through this layer have been discussed elsewhere (9, 18). The foregoing facts, together with the work reported by Schollenberger (15) and Robinson (14), indicate quite definitely that manganese exists in two states in the soil, namely, as exchangeable ions adsorbed by the colloidal complex, and as higher oxides of manganese. The equilibrium between these two forms depends largely upon the conditions existing in the soil. Since it has been shown earlier in this paper that $Mn(OH)_2$ may be transported to the cathode, and also that the partially hydrated oxides are more soluble under acid conditions, these facts may be utilized to explain why manganese as determined by electrodialysis is always greater than that extracted by neutral salts. During electodialysis the soil is subjected to increasing acid conditions, and therefore the equilibrium between the two forms of manganese is shifted in the direction of the more soluble form. When this stage is reached manganese may be transported to the cathode as ions or it may combine with acidoids and be transported as ionogens. The migration of either form of ionized manganese to the cathode will lead to its precipitation because of the high pH in the catholyte.

An illustration of the effect of increasing the acidity of the Colts Neck loam below the ultimate pH on the mobility of manganese is shown in table 3. The acidity was increased by adding a suspension of electrodialyzed humic acid containing 2.89 gm. of solids to 100 gm. of soil. The preparation and properties of this humic acid have been discussed elsewhere (18). The addition of this material has increased the mobility of manganese from 0.098 to 0.342 m.e. Similar results were obtained for iron and aluminum by Mattson (9) and by Toth (18). Other investigators have shown that the addition of organic matter increases the solubility of manganese in soils.

In the light of the foregoing discussion, it appears that manganese behaves, in some respects, like the basoids, iron and aluminum. When soil colloids are

TABLE 2

Release of manganese from some Coastal Plain soils during electrodialysis

PERIOD OF ELECTRODIALYSIS	TITRABLE BASES	Mn CONTENT OF CATHOLYTE	OBSERVATIONS ON CATHOLYTE
hours	*m.e* *	*m e.**	
	Sassafras loam		
0–4	0.616	0.0022	Clear
4–8	0.344	0.0056	Clear
8–12	0.243	0.0133	Slight sediment
12–16	0.020	0.0075	Slight sediment
16–20	0.000	0.0053	Very slight sediment
Total.....	1.223	0.0339	
	Sassafras sand		
0–4	0.445	0.0002	Clear
4–8	0.222	0.0058	Very slight sediment
8–12	0.061	0.0038	Very slight sediment
12–16	0.044	0.0017	Very slight sediment
16–20	0.044	0.0011	Very slight sediment
20–28	0.010	0.0002	Clear
Total.....	0.826	0.0128	
	Collington sandy loam		
0–4	1.698	0.0004	Clear
4–8	0.809	0.0047	Slight sediment
8–12	0.263	0.0156	Heavy sediment
12–16	0.081	0.0059	Slight sediment
16–20	0.044	0.0033	Slight sediment
20–28	0.020	0.0021	Very slight sediment
Total.....	2.915	0.0320	
	Colts Neck loam		
0–4	1.647	0.0010	Clear
4–8	0.788	0.0070	Clear
8–12	0.667	0.0170	Heavy sediment
12–16	0.303	0.0290	Heavy sediment
16–20	0.141	0.0220	Heavy sediment
20–28	0.060	0.0220	Heavy sediment
Total.....	3.606	0.0980	

* Per 100 gm. soil.

isoelectrically precipitated with iron and aluminum salts, a reduction in the cation exchange capacities of the colloids results. This is due to the combination of the basoid with the free valencies of the acidic fractions. In order to

determine whether manganese behaves in a like fashion, four sodium-saturated soil colloids (19) were isoelectrically precipitated with 1.5 millimoles of $MnCl_2$ solution in a total volume of 1 liter [isoelectric precipitation of $Mn(OH)_2$ was at pH 7.05 (11)]. The exchange capacity determinations of the manganated and original colloids are given in table 4. It is to be noted from this table that no marked effect on the exchange capacity from the added manganese was obtained with the Colts Neck or Cecil colloid, and only a slight reduction, with the two more siliceous colloids, the Sharkey and Sassafras. This slight reduction in exchange capacity is negligible in comparison with the

TABLE 3

Electrodialysis of Colts Neck loam with 2.89 gm. of Humic acid in relation to electrodialyzable manganese

PERIOD OF ELECTRODIALYSIS	TITRABLE BASES	Mn CONTENT OF CATHOLYTE	OBSERVATIONS ON THE CATHOLYTE
hours	*m.e.**	*m.e.**	
0–4	1.819	0.004	Clear
4–8	1.233	0.009	Light sediment
8–12	0.626	0.064	Very heavy sediment
12–16	0.101	0.190	Very heavy sediment
16–20	0.000	0.075	Very heavy sediment
Total.....	3.779	0.342	

* Per 100 gm. soil.

TABLE 4

Effect of isoelectric precipitation of manganese on the cation exchange capacity of soil colloids

COLLOID	SiO_2 / R_2O_3	CATION EXCHANGE CAPACITY	CATION EXCHANGE CAPACITY OF MANGANATED COLLOIDS	REDUCTION IN CATION EXCHANGE CAPACITY
		*m.e.**	*m.e.**	*m.e.**
Sassafras.....	3.37	0.206	0.181	0.025
Sharkey.....	2.72	0.650	0.610	0.040
Cecil.....	1.01	0.107	0.104	0.003
Colts Neck.....	0.81	0.319	0.319	0.000

* Per gram.

reduction in exchange capacity obtained by other investigators using iron and aluminum salts (10). This may be due to the instability of $Mn(OH)_2$ in alkaline solutions and to the effects of oxidation, leading to the formation of stable MnO_2 rather than $Mn(OH)_2$. Consequently with manganese in this form no direct combination between the acidoids can occur, and therefore no appreciable reduction in cation exchange capacity should be expected.

EFFECT OF LIMING ON MANGANESE IN SOILS

A clearer insight into the effect of lime on exchangeable and electrodialyzable manganese was obtained by studying the effect of $Ca(OH)_2$ additions to soils

partially saturated with manganese. Two soils were used for this purpose: a Sassafras loam having an exchange capacity of 5.79 m.e. per 100 gm., and a Penn silt loam having an exchange capacity of 13.89 m.e. The former soil contained 3.20 m.e. of exchangeable manganese, and the latter, 10.04 m.e., as shown by normal ammonium acetate extractions after partial saturation with manganese by leaching with $MnCl_2$ solution. These values were slightly higher as determined by extraction with 0.05 *N* HCl, being 3.53 and 10.78 m.e. respectively. By electrodialysis, the respective values were 3.89 and 10.23 m.e. The slightly higher values obtained by electrodialysis and by 0.05 *N* HCl are due to solubility effects upon the native manganese in these soils.

TABLE 5

Relation between lime applications and exchangeable and electrodialyzable manganese on two soil types

$Ca(OH)_2$ TREATMENT	pH OF SUPERNATANT LIQUID	$Ca(OH)_2$ IN SUPERNATANT LIQUID	Mn IN SUPERNATANT LIQUID	EXCHANGEABLE Mn BY *N* NH_4 ACETATE	EXCHANGEABLE Mn BY 0.05 *N* HCl	ELECTRODIALYZABLE Mn
		m.e.	*m.e.*	*m.e./100 gm.*	*m.e./100 gm.*	*m.e./100 gm.*
Sassafras loam						
None				3.20	3.53	3.89
Equivalent to one-half cation exchange capacity	7.15	0.18	0.06	2.24	2.73	3.65
Equivalent to cation exchange capacity	7.50	0.19	0.001	1.53	2.43	2.78
Equivalent to 2.0 times cation exchange capacity	9.70	0.42	Trace	0.82	2.23	2.88
Penn silt loam						
None				10.04	10.78	10.23
Equivalent to one-half cation exchange capacity	6.90	0.15	0.001	6.42	8.62	10.00
Equivalent to cation exchange capacity	8.07	0.23	Trace	2.75	6.46	6.60
Equivzlent to 2.0 times cation exchange capacity	11.90	2.14	Trace	1.46	5.20	6.61

The following procedure was used to study the effect of liming on the forms of manganese existing in the two soils partially saturated with manganese: 100 gm. of the soils were suspended in 750 cc. of solution containing $Ca(OH)_2$ in three different amounts. These quantities of $Ca(OH)_2$ corresponded to lime equivalents of one-half, one, and two times the cation exchange capacities of the soils. The soils were allowed to remain in contact with the solution for 2 days. At the end of this period, aliquots of the supernatant liquid were withdrawn, and determinations were made for soluble calcium, manganese, and pH. The soils were transferred to a large Büchner funnel, and the excess liquid was drawn off by suction. The soils were air dried and submitted to the normal ammonium acetate and the 0.05 *N* HCl extractions, as well as to electrodialysis.

The data for this experiment are reported in table 5. It may be seen that traces of manganese existed in the solutions even at pH values as high as 11.9. The exchangeable manganese by ammonium acetate decreased with increasing lime applications and pH. This is undoubtedly due to the exchange between the adsorbed manganese and calcium ions in the solution, resulting in precipitation of the former cation as insoluble $Mn(OH)_2$ which may be oxidized to MnO_2. For example, with the lowest treatment of lime on Penn silt loam, exchangeable manganese decreased from 10.04 m.e. per 100 gm. to 6.42 m.e., and with the highest lime treatment, to 1.46 m.e. Sassafras loam exhibited similar reductions. The exchangeable manganese by the 0.05 *N* HCl method was always higher than that obtained with the neutral salt method, as may be noted in the table. This may be accounted for by the solvent effect of the acid extractant upon the precipitated manganese complexes. In every case where the exchangeable manganese by the neutral salt method decreased, the exchangeable manganese by the 0.05 *N* HCl method increased in relation to the lime treatment. This indicates that where more of the original exchangeable manganese was precipitated as the hydroxide with increasing increments of lime, the solvent action of the acid extractant was more marked.

The contents of electrodialyzable manganese from these limed soils were greater than the values obtained by the neutral salt or 0.05 *N* HCl methods. The reasons for these higher values have already been discussed. It is of interest to note, however, that a maximum of only 6.6 m.e. of manganese per 100 gm. Penn silt loam and 2.88 m.e. per 100 gm. Sassafras loam was obtained from the two higher lime treatments.

INFLUENCE OF CALCIUM LIMESTONE AND DOLOMITIC LIMESTONE ON MANGANESE IN FIELD SOILS

The distribution of manganese in certain field plots as affected by lime treatment has been discussed by Blair and Prince (2), who showed that the total manganese content of the A_p horizon is generally higher than that of the lower horizons. In tables 6 and 7 the data on the distribution of total, exchangeable, and electrodialyzable manganese in the surface and subsoils of certain plots treated with various forms and amounts of lime are recorded.

The total, exchangeable, and electrodialyzable manganese content of the surface soils was found to be greater than that of the subsoils. The data presented in an earlier publication (13) on the soils of these plots indicate a definite accumulation of iron and aluminum in the subsoils under podzolization processes. This fact would lead one to suspect that manganese is not being transported to the lower horizons in the profile but is accumulating at the surface. This behavior of manganese in the profile is in line with our previous discussion earlier in the paper and the fact that Robinson (14) was unable to distinguish any other forms of manganese in the soil but manganese dioxide and manganese as exchangeable ions.

It would seem from the data in tables 6 and 7 that an actual conservation of total manganese occurs in the soil with the lime treatment. As pointed out

previously (13), however, the general data on these field plots point to an inherent difference between the plots. The behavior of manganese in soil from other plots of this series does not show this effect. For example, the data from the duplicate plots corresponding to the dolomitic limestone series

TABLE 6

Effect of limestone on exchangeable and electrodialyzable manganese in Sassafras loam

PLOT NUMBER	LIMESTONE TREATMENT	FIELD pH	ULTIMATE pH	TOTAL Mn	EXCHANGEABLE Mn BY *N* NH_4Ac	Mn BY ELECTRODIALYSIS
	*lbs.**			*m.e.*†	*m.e.*†	*m.e.*†
21 Top	None	5.03	4.42	0.761	0.030	0.034
22 Top	1000	5.27	4.22	0.902	0.029	0.091
23 Top	2000	5.62	4.44	0.987	0.023	0.084
24 Top	4000	6.36	4.33	1.268	0.029	0.156
21 Sub	None	5.24	4.42	0.705	0.012	0.029
22 Sub	1000	5.58	4.33	0.507	0.007	0.031
23 Sub	2000	5.96	4.55	0.536	0.012	0.026
24 Sub	4000	6.68	4.47	0.902	0.009	0.068

* Per acre.
† Per 100 gm. soil.

TABLE 7

Effect of dolomitic limestone on exchangeable and electrodialyzable manganese in Sassafras loam

PLOT NUMBER	DOLOMITIC LIMESTONE TREATMENT	FIELD pH	ULTIMATE pH	TOTAL Mn	EXCHANGEABLE Mn BY *N* NH_4Ac	Mn BY ELECTRODIALYSIS
	*lbs.**			*m.e.*†	*m.e.*†	*m.e.*†
21 Top	None	5.03	4.42	0.761	0.030	0.034
25 Top	1000	5.44	4.45	1.212	0.035	0.054
26 Top	2000	5.87	4.33	1.353	0.015	0.077
27 Top	4000	6.84	4.31	1.466	0.025	0.146
21 Sub	None	5.24	4.42	0.705	0.012	0.029
25 Sub	1000	5.73	4.39	0.902	0.016	0.041
26 Sub	2000	6.26	4.45	0.959	0.009	0.032
27 Sub	4000	7.08	4.43	1.000	0.014	0.052

* Per acre.
† Per 100 gm. soil.

described in table 7 showed a uniform content of total manganese, namely, 1.10 m.e. per 100 gm.

The exchangeable manganese content of the soils did not indicate a definite correlation with the lime treatment either in the surface or in the subsoils. The values for exchangeable manganese ranged from 0.007 to 0.03 m.e. per 100 gm. The lack of correlation between the data from the field and that obtained in the laboratory, where the influence of $Ca(OH)_2$ addition upon

exchangeable manganese was studied, may be due to the fact that under field conditions it is impossible to control all factors rigidly.

The electrodialyzable manganese generally increased with the limestone applications. Gilligan (5) has noted that limed soils contain more electrodialyzable manganese than unlimed soils, and the results in tables 6 and 7 are in line with his findings. An examination of the data in tables 6 and 7 would seem to indicate a correlation between the total and electrodialyzable manganese. That no such correlation exists may be seen from the electrodialyzable manganese content of certain plots that have a fairly uniform content of total manganese. The data that follow are given for only the surface soils of the corresponding series reported in table 7:

DOLOMITIC LIMESTONE TREATMENT	PLOT NUMBER	TOTAL Mn	ELECTRODIALYZABLE Mn
lbs./A.		*m.e./100 gm.*	*m.e./100 gm.*
None	21	0.76	0.034
1000	39	1.10	0.027
2000	40	1.10	0.042
4000	41	1.10	0.094

The behavior of the electrodialyzable manganese on these field soils is in line with the data presented in table 5 where a similar study was made under laboratory conditions.

SUMMARY

The behavior of manganese in soils under laboratory and field conditions was studied.

An attempt was made to clarify the electrodialytic behavior of solutions of $MnCl_2$ and soils containing adsorbed manganese. It was shown that adsorbed manganese can be released quantitatively from soils by electrodialysis.

The release of manganese from some cultivated Coastal Plain soils of New Jersey by electrodialysis was studied. A similarity was observed between the release of manganese, iron, aluminum, and magnesium under these conditions. The mobility of manganese increased in the later stages of electrodialysis as the pH of the soil decreased. The transport of manganese was primarily as ionogens rather than as ions.

Manganese appeared to exist in the soils as exchangeable ions and ionogenic complexes. The equilibrium between these two forms of manganese was affected by soil conditions. The addition of humic acid to Colts Neck loam resulted in a greater release of manganese.

The isoelectric precipitation of $Mn(OH)_2$ with sodium-saturated soil colloids did not reduce to any extent the cation exchange capacity of the colloids.

Soils that were partially saturated with manganese were used to study the effect of lime on exchangeable and electrodialyzable manganese. It was shown that as the lime applications increased the exchangeable manganese decreased. The values for the electrodialyzable manganese always exceeded

the exchangeable. This was due to the fact that electrodialyzable manganese represented the sum of exchangeable manganese and manganese transported as ionogenic complexes. It was also shown that manganese in the latter form is nonexchangeable but is soluble to some degree in 0.05 *N* HCl.

The data obtained with field soils were interpreted from the viewpoint of the laboratory experiments and confirmed the laboratory findings. It was also pointed out that the surface soils contained more total manganese than did the subsoils.

REFERENCES

(1) Association of Official Agricultural Chemists 1935 Official and Tentative Methods of Analysis. Washington, D. C.

(2) Blair, A. W., and Prince, A. L. 1936 Manganese in New Jersey soils. *Soil Sci.* 42: 327–333.

(3) Britton, H. T. 1932 Hydrogen Ions. D. Van Nostrand Co., New York.

(4) Conner, S. D. 1932 Factors affecting manganese availability in soils. *Jour. Amer. Soc. Agron.* 24: 726–733.

(5) Gilligan, G. M. 1936 The effect of fertilizers and liming upon the electrodialyzable manganese of a Sassafras silt loam. *Soil Sci.* 41: 203–208.

(6) McCool, M. M. 1934 Effect of various factors on the soluble manganese in soils. *Contrib. Boyce Thompson Inst.* 6: 147–164.

(7) Mann, H. B. 1930 Availability of manganese and iron as affected by application of calcium and mangnesium carbonates to the soil. *Soil Sci.* 30: 117–141.

(8) Mattson, S. 1926 Electrodialysis of the colloidal soil material and the exchangeable bases. *Jour. Agr. Res.* 33: 552–567.

(9) Mattson, S. 1933 Laws of soil colloidal behavior: XI. Electrodialysis in relation to soil processes. *Soil Sci.* 36: 149–163.

(10) Mattson, S., and Hester, J. B. 1935 The laws of soil colloidal behavior: XV. The degradation and regeneration of the soil complex. *Soil Sci.* 39: 75–84.

(11) Mattson, S., and Pugh, A. J. 1934 The laws of soil colloidal behavior: XIV. The electrokinetics of hydrous oxides and their ionic exchange. *Soil Sci.* 38: 299–313.

(12) Prince, A. L., and Toth, S. J. 1937 Electrodialysis and cation exchange studies on soils of varying organic matter content. *Soil Sci.* 43: 205–217.

(13) Prince, A. L., and Toth, S. J. 1937 Effect of long continued use of dolomitic limestone on certain chemical and colloidal properties of a Sassafras loam soil. *Proc. Soil Sci. Soc. Amer.*, 1937: 207–214.

(14) Robinson, W. O. 1929 Detection and significance of manganese dioxide in the soil. *Soil Sci.* 27: 335–350.

(15) Schollenberger, C. J. 1928 Manganese as an active base in the soil. *Soil Sci.* 25: 357–358.

(16) Schollenberger, C. J. 1930 Effect of leaking natural gas upon the soil. *Soil Sci.* 29: 261–266.

(17) Schollenberger, C. J., and Dreibelbis, F. R. 1930 Effect of cropping with various fertilizers, manures and lime treatment on the exchangeable bases of plot soils. *Soil Sci.* 29: 371–384.

(18) Toth, S. J. 1937 Anion adsorption by soils and soil colloids in relation to changes in colloidal properties and plant growth. Thesis, Rutgers University, New Brunswick, N. J.

(19) Toth, S. J. 1937 Anion adsorption by soil colloids in relation to changes in free iron oxides. *Soil Sci.* 44: 299–314.

(20) Willis, L. G. 1932 The effect of liming soils on the availability of manganese and iron. *Jour. Amer. Soc. Agron.* 24: 716–726.

THE MOVEMENT OF WATER IN HEAVY SOILS AFTER IRRIGATION

E. C. CHILDS[1]

School of Agriculture, University of Cambridge, England

Received for publication February 8, 1938

The theory of diffusion of water through soil (2), developed in connection with the drainage of heavy clay soils in humid climates (7), has been shown to be in agreement with the behavior observed (3) in artificially prepared columns of soil material investigated by various workers (1, 8, 9). The application of the theory to similar soils in more arid climates where irrigation is the rule, is of special interest. Not only is the computation of penetration of water of direct importance, but the zones of irrigation provide the most favorable conditions for testing the theory by experiments in the field. It need hardly be stressed that such field experiments are essential, since it is impossible to prepare adequate lysimeters at reasonable cost without disturbing the natural structure of such soils and thereby profoundly modifying their drainage properties. Field experiments are not easy in a region of variable and only approximately predictable weather, such as the British Isles, because the theory can be developed, on account of mathematical difficulty, only for certain steady surface conditions. Moisture movements in heavy soils are so slow that such steady conditions must be maintained for a considerable length of time before one can observe changes of moisture content which are large in comparison with the errors involved. The controlled applications of water during periods of very settled weather, associated with irrigation, render the regions where such operations are carried out peculiarly suitable for our purpose. They have the added advantage that the application of a large quantity of water in a short time produces a moisture profile having a steep gradient at considerable depth. This means, as we shall see, that water movements are to be observed in a medium which is fairly uniform and free from surface disturbances.

Fortunately, a region of the type described, enjoying well-defined seasons and steady weather, has been the home of experiments on moisture movements in clay soils (4), and data of a nature suitable for the application of diffusion theory are available. Greene, working in the Eastern Gezira where the soil is a heavy clay of alkaline reaction, has published a number of moisture profiles in connection with irrigation practice, and some of these have been chosen as the material for the present discussion.

[1] It is a pleasure to acknowledge the unstinted help afforded me by H. Greene and O. W. Snow, who have freely put at my disposal unpublished data from the Agricultural Research Station at Wad Medani, in the Eastern Gezira.

The basis of the diffusion theory, recapitulated, is the assumption that the rate of flow of soil moisture at a given point in a given direction is proportional to the gradient of the moisture profile in that direction. The justification for this assumption has been previously discussed (2, 7). Thus if one expresses the mass of soil water per unit volume of soil as a fraction c of the mass of dry matter, σ, per unit volume, then the rate of flow, $\frac{\partial Q}{\partial t}$, in the direction x is proportional to $\frac{\partial c}{\partial x}$, i.e.,

$$\frac{\partial Q}{\partial t} = -k \frac{\partial c}{\partial x} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (A)$$

where k is a constant of proportionality and is called the "diffusion coefficient." Starting with a knowledge of k, σ, and the initial moisture profile, however complicated, we can calculate the subsequent moisture profile at any time for certain conditions of water control. In particular, if we identify x with depth and assume horizontal planes to be surfaces of equal moisture content, and imagine that the soil surface is maintained at constant wetness (for example, at saturation by means of irrigation or at air-dryness by rapid evaporation), then the moisture profile c_t at time t is given by the expression:

$$c_t = c_s + \sum_n \left(\frac{2}{l} e^{-\frac{k}{\sigma}\left(\frac{n\pi}{2l}\right)^2 t} \int_0^l (c_0 - c_s) \sin \frac{n\pi x}{2l}\, dx \right) \sin \frac{n\pi x}{2l} \quad \ldots (B)$$

$$(n = 1, 3, 5, 7, \ldots)$$

where c_s is the constant surface moisture content, c_o the initial profile, and l is the total depth of the soil in which water diffusion is taking place.

If we assume, instead, that there is no arrival or departure of water from the soil as a whole, but only redistribution of such water as is already in it, we have now:

$$c_t = \frac{1}{l} \int_0^l c_0\, dx + \sum_n \left(\frac{2}{l} e^{-\frac{k}{\sigma}\left(\frac{n\pi}{l}\right)^2 t} \int_0^l c_0 \cos \frac{\pi n x}{l}\, dx \right) \cos \frac{\pi n x}{l} \quad \ldots (C)$$

$$(n = 1, 2, 3, 4, \ldots)$$

The conditions leading to equation (B) are of importance in connection with drainage in humid climates, when rainfall maintains the surface of heavy soil in a state approximating saturation, and also in arid climates during the period following irrigation, when the heat from the sun tends to maintain the surface, at least during the day, in a condition of air-dryness. Hence, using the appropriate equation, we can calculate a moisture profile for comparison with the one observed at the end of the given interval or intervals of time, and the extent of the agreement between the two is the evidence for the soundness of the theory. It will be seen that the analysis involves the evaluation of certain

definite integrals of functions of the depth, and the range over which these must be taken is, to be rigid, the whole depth of the soil deposit. In practice we make only negligible errors in limiting the range to that depth in which water movement is known to be greater than the errors of measurement.

EXPERIMENTAL DATA

Two of Greene's sets of experiments contain sufficient material of the nature required for our purposes. These are (*a*) the investigation of the soil-moisture profiles at various dates after irrigation and (*b*) the examination of the effect of applications of gypsum on the depth of penetration of water. The curves are not entirely satisfactory for our purpose, since the experiments were carried out with other ends in view, but we shall see that they are adequate when one considers the approximate sort of agreement with theory which can be legitimately expected from such a nonuniform medium as a field soil 6 or more feet deep. In each experiment the moisture content at various depths shortly after irrigation is given, and from this information the moisture profiles were obtained by drawing the smoothest possible curves through the points given by plotting moisture content against depth. These are shown as the solid line curves in figures 1 to 5, in which the experimental points are generally omitted in order to avoid confusion with observed values on subsequent occasions.

Starting with these initial profiles, we must, in calculating subsequent profiles, first decide upon the proper conditions to be assigned to the surface. It must be admitted that the actual state of affairs is so complicated that a rigid solution of the diffusion equations is out of the question. We must choose conditions which permit of a solution if we are to progress farther, yet these must be a sufficiently good approximation to the truth if the calculations are to be of more than academic interest. Immediately following irrigation, when the soil at the surface is very wet, it is likely that the rate of evaporation is limited by the rate of absorption of heat from the sun, and the appropriate boundary condition is then that the rate of loss of water from the surface, averaged over each day, is constant. This state of affairs cannot last very long, and must be succeeded by one in which the rate of evaporation is limited by the maximum rate at which water can reach the surface from the soil below. Because of the slowness of water movements in heavy soils, this maximum rate may be so low that the sun is able to maintain the surface in a state of air-dryness; the gradually decreasing rate at which water reaches the surface is just balanced by the rate at which it leaves the surface in the form of vapor. When these latter conditions set in, the pressure of the water vapor at the surface must be low, and consequently evaporation can take place within the soil, the vapor thus produced diffusing upward through the drier layers (down the vapor-pressure gradient) and so to the outside air. In this way the actual water loss is doubtless greater than that accounted for by diffusion of water in the liquid state, with the assumed boundary conditions. Hence if we assume, as the general trend of the published profiles would lead us to suppose,

that the soil surface is maintained throughout the drying period in a state of air-dryness, we shall probably overestimate the loss of water in the early part of the period and underestimate it in the latter part. We may, therefore, expect our calculations to provide a final profile which is not very far from the truth, the more so because, as will be shown, rather large variations in the surface conditions have only a minor effect on the changes in the moisture profile at considerable depth, where our interest is chiefly centered.

Our arguments lead us, therefore, to choose equation (*B*) as that appropriate to the case. The only question remaining to be settled is the correct value to be assigned to the surface moisture content, c_s. Greene (4) gives figures of 14 per cent and 6 per cent respectively for the hygroscopic coefficient and air-

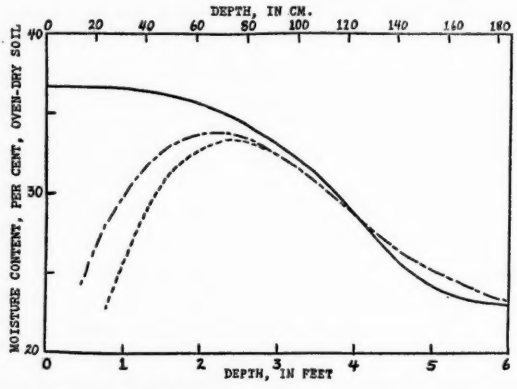

FIG. 1. MOISTURE PROFILES ILLUSTRATING EFFECT OF DIFFERENT SURFACE CONDITIONS ON THE CALCULATED PROFILES FOR EASTERN GEZIRA SOIL

———— Initial profile.

— — — — Calculated subsequent profile, surface maintained at 14 per cent moisture.

---------- Calculated subsequent profile, surface maintained at 0 per cent moisture.

It will be observed that the difference is negligible below about 2 feet.

dry moisture content of Gezira soil. It might be thought that the surface soil, being in contact with moister lower soil, should not dry out to such a low moisture content as the air-dry value, yet one at least of the observed profiles tends to a moisture content of zero at the surface. Because of this uncertainty, calculations were made to illustrate the difference between the effects of maintaining the surface at 14 per cent moisture and at zero moisture. The result is shown in figure 1, the initial profile being that observed by Greene 6 days after irrigation (4, fig. III) and with a trial value of $\frac{k}{\sigma}$. When the true value of $\frac{k}{\sigma}$ finally decided upon is taken, the calculated profiles correspond to a time interval of about 40 days. It will be seen that the difference to be expected

is confined to the top 2 feet, a region in which we are not primarily interested. Hence it is not a serious matter if we make an indifferent judgment of the surface conditions within the possible limits. In the present paper a value of zero has been assigned to c_s where this has seemed to be the case, and a value of 14 per cent where this has been judged proper; in no case does this difference affect the results except near the surface.

COMPARISON OF OBSERVED AND CALCULATED PROFILES

We deal first with the profiles showing the movement of water in plots receiving various applications of gypsum. The control plots are neglected

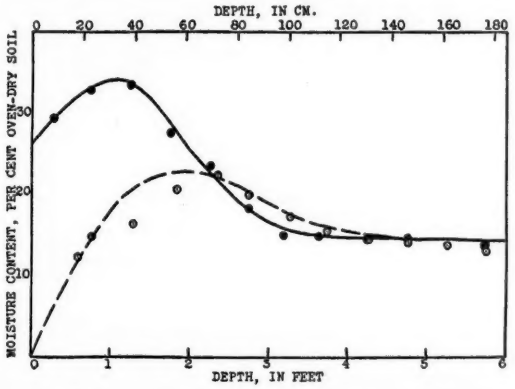

FIG. 2. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 1 TON OF GYPSUM PER ACRE HAD BEEN APPLIED

Values of constants used for the calculations are $\frac{k}{\sigma} = 3.0$, $c_s = 0$.

———— Initial profile, April 1927.
● ● ● Observed points from which the initial profile was drawn.
— — — Calculated profile, October 1927.
⊙ ⊙ ⊙ Observed values, October 1927.

because, in the untreated soil, the steeply sloping parts of the initial profile where moisture movements may be expected to be at a maximum are within the top 2 feet, and hence the moisture movements in which we are interested take place in a region which is subjected to the masking influences and the uncertainties of calculation which we have discussed. In figure 2 is shown the initial profile, taken in April 1927, for the plots to which 1 ton of gypsum per acre had been applied, together with the experimental points from which the initial profile was drawn. The profile calculated for October 1927 is shown together with the observed points for this date for comparison. Greene also publishes a profile taken in December 1927, but it is not profitable to attempt to calculate a profile because water was applied shortly before this profile was

observed, the surface conditions thereby being drastically changed. This point will again be referred to in the discussion. It is sufficient to remark here that this December profile is consistent with the view that the deeper soil had gained more water at the expense of the upper layers, in accordance with the diffusion laws, but the subsequent irrigation had made good the losses suffered by these upper regions.

The behavior of plots having a dressing of 4 tons of gypsum per acre differs from that of all the others in that the soil at all depths loses moisture, instead of the dry lower soil's gaining at the expense of the upper moistened soil. If we examine figure 3, we see that the shape of the October profile is what we should expect but that there is a displacement bringing it wholly below the

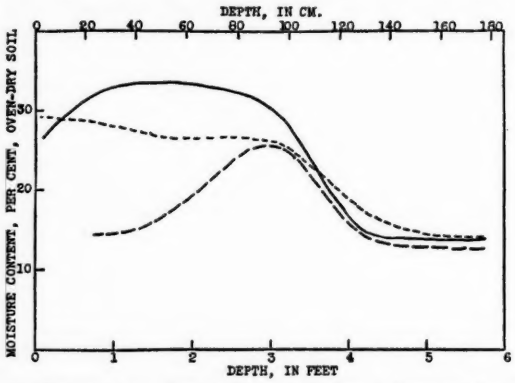

FIG. 3. MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 4 TONS OF GYPSUM PER ACRE HAD BEEN APPLIED

———— Initial profile, April 1927.
— — — Subsequent profile, October 1927.
---------- Subsequent profile, December 1927.

initial April profile instead of there being an intersection at a depth of about 3.5 feet and an asymptotic approach at greater depth. Calculations for this anomalous case were not made, but by comparison with the calculated curves in figures 2 and 4 it can be seen that the theoretical profile would be closely similar to the observed December profile. This also will be discussed later, but the anomaly may be no greater than can be accounted for by experimental error, since there was only fourfold replication of plots and the changes of moisture content in which we are interested do not amount to more than 2 or 3 per cent of the weight of dry matter.

In figure 4 is shown the behavior of the plots to which 10 tons of gypsum per acre was applied. The previous remarks apply here. This calculated profile is also in rather better agreement with the December profile than with that for

April, for which it was computed. The bodily shift of the April profile is not so pronounced, however, as in figure 3. The value adopted for $\frac{k}{\sigma}$ in the foregoing calculated profiles was 3.0, where the units of length, mass, and time are the centimeter, the gram, and the day respectively.

A more stringent test of the theory is provided by figure 5. Here, starting with a profile taken 6 days after irrigation, two subsequent profiles can be calculated and compared with those observed, one being for a short time-interval (26 days after irrigation) and the other being observed 120 days after irrigation. The sampling, even though carried to a depth of 6 feet, did not

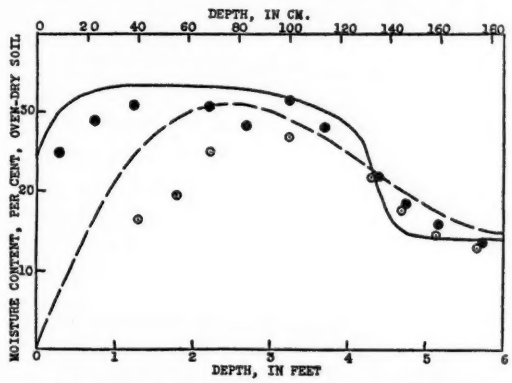

FIG. 4. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES FOR GEZIRA SOIL TO WHICH 10 TONS OF GYPSUM PER ACRE HAD BEEN APPLIED

The observed points from which the initial profile has been drawn are omitted to avoid confusion. $\frac{k}{\sigma}$ 3.0, $c_s = 0$.

———— Initial profile, April 1927.
— — — Calculated profile, October 1927.
⊙ ⊙ ⊙ Observed values, October 1927.
● ● ● Observed values, December 1927.

reach a region where moisture redistribution was negligible. It was therefore necessary to extrapolate the initial profile to a depth of 12 feet (366 cm.) and to a moisture content which seemed reasonable and probable. This extrapolation to a moisture content of 22 per cent at 12 feet is merely a necessity for the calculations and is of no interest in the discussion; it is therefore not shown in figure 5, which ends at the limit of observations, at a depth of 6 feet. The experiments were carried out on good soil at the Gezira Research Farm, whereas the preceding ones were on poor soil at Ganib. It was accordingly found necessary to choose a new value for $\frac{k}{\sigma}$ for this soil, and by trial and error a value

of 16.0 was selected. It will be seen that the agreement between observed and calculated profiles is very fair below a depth of about 3 feet. It is possible that agreement extends upwards into the second foot from the surface, since the depression in the observed profiles, which occurs in the third foot through-

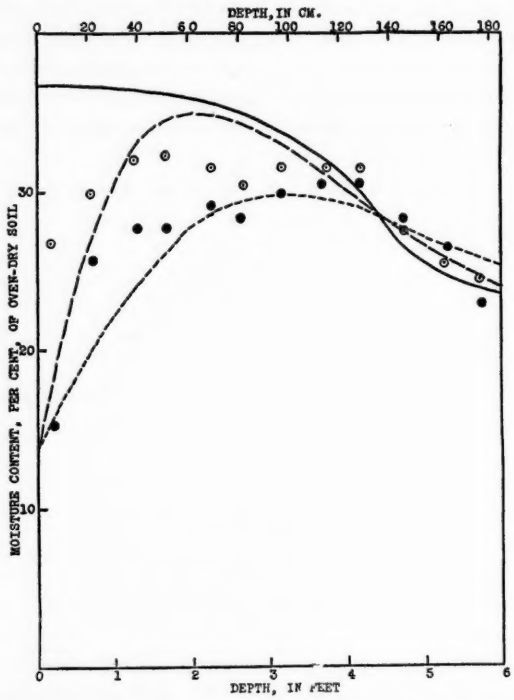

FIG. 5. COMPARISON BETWEEN OBSERVED AND CALCULATED MOISTURE PROFILES AT VARIOUS INTERVALS AFTER IRRIGATION

$\frac{k}{\sigma}$ 16.0, c_s = 14.0 per cent.

———— Initial profile, 6 days after irrigation.
— — — Calculated profile, 26 days after irrigation.
⊙ ⊙ ⊙ Observed values, 26 days after irrigation.
---------- Calculated profile 120 days after irrigation.
● ● ● Observed values 120 days after irrigation.

out the series, is due to the fact that the moisture contents are expressed as a percentage of the mass of dry soil matter, and the density of this, according to Greene, reaches a maximum in the third foot. If due consideration is given to the long intervals of time involved and the consequent possibility of changes of atmospheric conditions during the experiment (the experiments of figures 2

to 4 include, in fact, the summer rains in the "drying" period), to the fact that we are applying a theory developed for a homogeneous medium to a field soil and not to a laboratory mixture of artificial homogeneity, and finally to the fact that measurements of moisture profiles are subject to considerable errors, it would seem that the general agreement between observation and theory may be regarded as satisfactory.

DISCUSSION

The movements of water with which we have been dealing are of interest in connection with irrigation mainly in the study of the slow penetration during the long period following flooding. During the early part of the flood period, when the greater part of the water is taken up by the soil but does not penetrate much below the surface zone, movement is rapid and obeys other than diffusion laws. Water is applied when the soil is dry and therefore cracked, in places to a great depth. The first applications are observed to rush down these cracks under the force of gravity and presumably to spread almost equally quickly into the minor cracks and interspaces between the clods and crumbs. As this water is taken up, the soil swells, eventually the water passages close, and further movements are of the slow diffusion type. The mechanism by which the soil aggregates absorb the water from the interspaces may, of course, be of a diffusion nature, but this final stage is of only minor importance; it remains true that the presence of the water at the depth at which it is absorbed into the soil is accounted for by mass movement down the cracks under the force of gravity. When this early period is over and the swelling has closed the cracks, we may expect to observe further and much slower mass movements from one depth to another due to diffusion, unmasked by the rapid gravitational movements.

The behavior of gypsum as a soil improver, as indicated in figures 2 to 4, may be examined in the light of these observations. We first notice that the same value of the coefficient of diffusion holds for all the various applications of gypsum, and consequently that the slow penetration is in no way improved by such applications. The most obvious effect is on the rapid uptake of water during flooding, and here we see that increasingly heavy dressings of gypsum have the effect of steepening the "step" in the moisture profile and of shifting it to greater depths. Israelsen (5) has shown that such differences are characteristic of the change from heavy to light soil. It may be that replacement of the sodium, which occurs in the Gezira soils in notable quantities, by the calcium ion is accompanied by oriented coagulation, as has been suggested by Marshall (6), and an increase in size of the primary particles of the clay fraction; but, in any case, it is known that the calcium clay is more stable and swells less than does clay which contains appreciable quantities of exchangeable sodium. Hence crumbs and aggregates in general would tend to be more stable and the cracks and interspaces more persistent. In terms of coagulation, the closer binding of the clay particles has eliminated some of the minute

pore spaces in which diffusion occurs to the benefit of the major spaces. The cracks provide direct passages between the deeper soil and the outside air, particularly when the drying of the soil has caused the cracks to open slightly; and hence we must admit the possibility, as we have seen, of water loss, even at depth, by direct evaporation. At the same time the cracks, being chiefly in the vertical direction, would not tend to prevent the movement of water from one depth to another by diffusion; hence, we might expect two superimposed effects.

Examination of figures 2 to 4 shows that the observed water movements are consistent with the view of two superimposed effects outlined. The soil to which little gypsum was added gives moisture profiles which are in excellent agreement with the profiles calculated from the simple theory. With heavier dressings, however, there is a loss of moisture throughout the profile during the period April–October, in addition to a redistribution in accordance with diffusion laws. The effect is to give a profile which agrees in shape with the calculated one but is displaced downwards (i.e., in the direction of dryness). This loss must be accompanied by shrinking and cracking of the soil, so that reflooding might be expected to make good this loss almost instantaneously. The December profiles, taken shortly after such a reflooding, shows that this indeed happens, the whole curve of the profile being shifted to be in better agreement with that calculated. There is a rapid response to flooding even at a depth of 5 or 6 feet, whereas the first flooding penetrated quickly only to a depth of 3 or 4 feet. Behavior in the upper 2 feet is, as we have shown, wholly outside the scope of the simple theory.

In figure 5 we have omitted the profile observed 256 days after irrigation because the loss of moisture throughout the whole depth due to evaporation outweighs changes due to diffusion. The importance of the curves shown lies in their evidence of the continuous nature of diffusion. There is no indication of a final steady state differing from uniformity of moisture content, as has sometimes been supposed. A progressive movement of moisture takes place from the wetter to the drier soil. The actual value of the coefficient of diffusion may change with moisture content, i.e., it might have been possible to obtain better agreement between the calculated and observed profiles for the 26-day and 120-day periods separately by adopting a different value for each case, but the agreement shown indicates that such a change cannot be considerable in the range of moisture contents found under field conditions.

SUMMARY

An application of the theory of diffusion of water in heavy soils has been made to observations taken under irrigation conditions. It is shown that diffusion can account for the slow movements after irrigation and can be important in soil amelioration, but that during flooding such movements are masked by the more rapid gravitational movement.

REFERENCES

(1) ALWAY, F. V., AND CLARK, V. L. 1911 A study of the movement of water in a uniform soil under artificial conditions. *Nebr. Agr. Exp. Sta. Ann. Rpt.* 1911: 246–287.

(2) CHILDS, E. C. 1936 The transport of water through heavy clay soils: I. *Jour. Agr. Sci.* 26: 114–127.

(3) CHILDS, E. C. 1936 The transport of water through heavy clay soils: III. *Jour. Agr. Sci.* 26: 527–545.

(4) GREENE, H. 1928 Soil permeability in the Eastern Gezira. *Jour. Agr. Sci.* 18: 531–543.

(5) ISRAELSEN, O. W. 1917 Studies on capacities of soils for irrigation water, etc. *Jour. Agr. Res.* 13: 1–36.

(6) MARSHALL, C. E. 1930 Orientation of anisotropic particles in an electric field. *Trans. Faraday Soc.* 26: 173–189.

(7) NICHOLSON, H. H., AND CHILDS, E. C. 1936 The transport of water through heavy clay soils: II. *Jour. Agr. Sci.* 26: 128–141.

(8) SHAW, C. F. 1927 The normal moisture capacity of soils. *Soil Sci.* 23: 303–317.

(9) VEIHMEYER, F. J. 1927 Some factors affecting the irrigation requirements of deciduous orchards. *Hilgardia* 2: 125–291.

A FIELD OUTFIT FOR DETERMINING THE MOISTURE CONTENT OF SOILS[1]

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication March 14, 1938

It has been shown[2] that the moisture content of mineral soils containing less than 11 per cent of organic matter can be determined accurately and rapidly by means of the burning-alcohol method. In a series of comparative studies it was definitely proved that for such soils this method is as accurate as the standard oven-drying method, and that with the burning-alcohol method the moisture content of sands can be determined in from 5 to 10 minutes, of loams in from 10 to 20 minutes, and of clays in from 10 to 35 minutes, depending on their water content and their permeability to alcohol. In the report offering the method, technique and experimental data showing accuracy were presented. No attempt was made to apply the method to field conditions.

The method has since received further study with the object of applying it to field conditions. It is the purpose of this paper to present a field outfit that has been devised, by means of which the burning-alcohol method can be conveniently used to determine the moisture content of soils under field conditions.

DESCRIPTION OF OUTFIT

This field outfit is shown in plate 1. It is a box 26 inches high 16 inches wide, and 7 inches deep, made of light galvanized iron and having two compartments. The lower compartment is a container for the necessary equipment. Its door consists of a metal sheet which slides from right to left in grooves. The upper compartment serves chiefly for housing the triple beam balance and protecting it from the wind. The two sliding doors to this compartment have glass windows which allow the operator to see and to adjust the weights accurately and which at the same time protect the balance from the wind. The glass is synthetic and is very light in weight and resistant to breaking. When the outfit is being carried, a metal sheet slides over the doors to protect the glass windows as well as to hold them in place. On the top of the box is a groove into which is inserted the door to the lower compartment, and

[1] Authorized for publication by the director as journal article No. 321 n.s.

[2] Bouyoucos, G. J. 1937 Evaporating the water with burning alcohol as a rapid means of determining moisture content of soil. *Soil Sci.* 44: 377–383.

thus is formed a platform where the soils can be dried by the burning-alcohol procedure.

For use in connection with this field outfit, a high-grade triple beam balance[3] is recommended. The balance is held firmly in place in the compartment; and since it is well protected from the wind, it functions with as high a degree of accuracy as it does in the laboratory.

The box when standing on the ground, is high enough for the comfortable operation of the balance by a person of normal height seated on a camp stool. On the other hand, various arrangements could be made to raise the box to suit the operator's comfort and convenience.

The soils are dried by means of burning alcohol, in a set of two cups, as shown in the lower compartment of the box (pl. 1, fig. 1). The smaller cup is made of copper, and the larger one of aluminum. The smaller cup is 2 inches in diameter, $\frac{3}{4}$ inch deep, with perforated bottom, and resting on four legs $\frac{3}{8}$ inch high. The larger cup is 3 inches in diameter, 1 inch deep, and has a solid bottom. The smaller cup, which contains the soil, is always kept in the larger cup in order that no soil will be lost during treatment with the alcohol and during weighing.

PROCEDURE

The procedure for making a moisture determination consists, first, of laying a filter paper in the bottom of the smaller cup, placing this cup in the larger one, and weighing them together. During the entire procedure the cups are always kept one inside the other and are always weighed together as a single unit. A layer of soil about $\frac{1}{2}$ inch thick, amounting to about 20–30 gm., is placed in the small cup, and the cups are weighed again. About 25 cc. of pure methyl alcohol is then poured gradually on top of the soil layer, and after most of it has drained through the soil, it is ignited. After the alcohol is burned and the flame goes out, the cups are weighed a third time. In order to be certain that all the water in the soil is expelled, about 10 cc. more alcohol is poured into the large cup and burned, and the cups are again weighed. This procedure of burning small quantities of alcohol in the large cup and of re-weighing is repeated until the weight becomes constant. As a rule, more than two alcohol burnings are necessary to dry the soil completely. Several burnings are necessary for a soil of high moisture content. With such soils, it is not necessary to weigh the cups until several portions of alcohol are burned.

It was found experimentally that the soil can be dried more rapidly, and with considerably less consumption of alcohol, by adding several small amounts of alcohol than by adding a very large amount at the outset. This is partly due to the fact that when a small amount is used the flame tends to get under the soil cup and heat the soil. Since the alcohol is not explosive, it can be poured into the large cup while there is still some flame. In order to eliminate the tedious procedure of measuring out the small portions of alcohol, a special

[3] Catalog no. 1966, Arthur Thomas & Co.

mark has been made in the large cup to indicate a 10 cc. volume of alcohol. The supply of alcohol, therefore, can be kept in a bottle, and by means of a syphon arrangement, the small additions of alcohol can be measured into the cup.

COMMENTS

As shown in the first report, the moisture content of mineral soils containing less than 11 per cent of organic matter can be determined as accurately by the burning-alcohol method as by the standard oven-drying method. This follows logically from the fact that the soil is repeatedly dried with burning alcohol until its weight becomes constant.

In the field, as in the laboratory, the rapidity of the method for determining soil moisture depends upon the water content of the soil and upon the extent to which the alcohol extracts the water as it percolates through the soil. It is quicker to evaporate the water when it is dissolved in alcohol than when it is in the soil. To determine the moisture content of soils that are readily permeable, such as the sands, and even the clays in the granular condition and of low moisture content, takes about 5 to 15 minutes, including the time for weighing. Soils that have a very high moisture content, especially if they are impermeable, such as heavy puddled clays, require from 10 to 35 minutes for moisture determination. On the other hand, work may be carried forward on a number of soils at the same time, as the procedure does not require constant attention.

SUMMARY

An outfit has been devised, which can easily be carried into the field, for the accurate and rapid determination of the moisture content of soils by means of burning alcohol.

PLATE 1

FIELD OUTFIT FOR DETERMINING MOISTURE CONTENT OF SOILS BY THE BURNING-ALCOHOL METHOD

FIG. 1. Open view of the box with glass windows.

FIG. 2. Closed view of box.

(Manufactured and handled by the Wood and Metal Products Company, Bloomfield Hills, Michigan.)

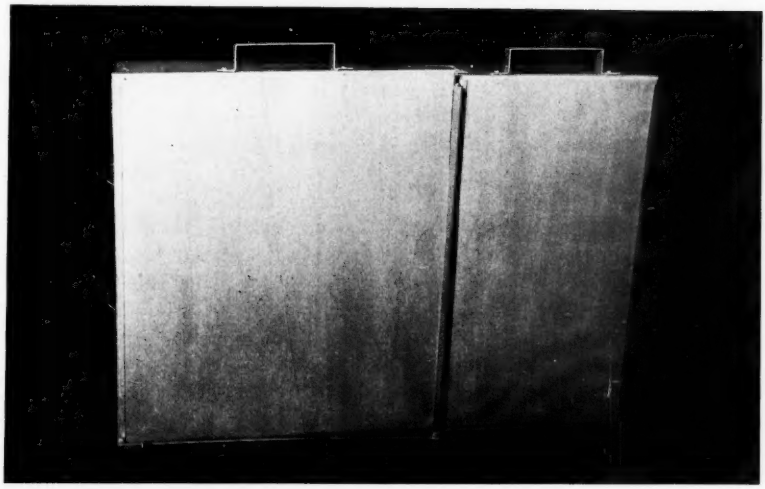

FIG. 2

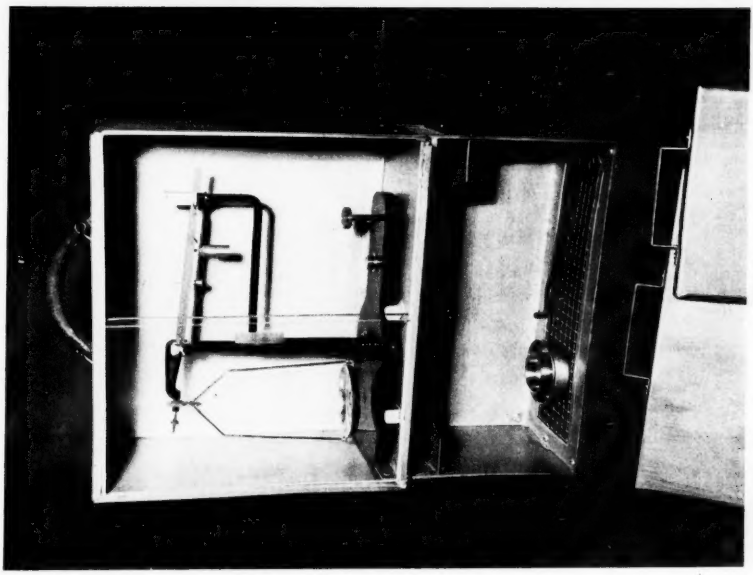

FIG. 1

HYDROGEN-ION ACTIVITY OF COLLOIDAL ACIDS IN SOILS

AMAR NATH PURI AND A. N. DUA

Irrigation Research Institute, Lahore, India

Received for publication June 18, 1937

It is well known that acids have a quantity factor as well as an intensity factor. The former is determined by the total hydrogen capable of being replaced by a metal; and the latter, by the number of hydrogen ions present, i.e., the dissociation or activity coefficient of the acid. The direct measurement of hydrogen-ion concentration of soils colorimetrically or electrometrically is a well-known method, but sufficient attention has not so far been paid to the methods of measuring catalytic activity of hydrogen ions in soil colloids. The two best known methods of measuring concentration of hydrogen ions by their catalytic activity are hydrolysis of ethyl acetate and inversion of sucrose. These are dealt with in separate sections of this paper.

HYDROLYSIS OF ETHYL ACETATE

Parker and Bryan (5) compared the inverting and hydrolyzing power of acid soils with sucrose and with ethyl acetate, respectively, both with suspension and with water extract. They found that hydrolysis of ethyl acetate was greatest in water extract and least in soil suspension; on the other hand, sugar inversion was greatest in soil suspension and least in water extract. They concluded, therefore, that acid silicates catalyze the inversion of cane sugar and not the hydrolysis of ethyl acetate, which is brought about only by a higher concentration of H ions in the mass of the soil solution. These authors considered the possibility of a partial neutralization of the acetic acid by its action on the minerals of the soil but thought it would not account for the extremely small hydrolysis brought about by soil suspensions.

When the large amount of exchangeable bases, even in acid soils, is considered, the possibility is by no means remote that almost the whole of the acid would be used up by the soil when the hydrolysis takes place in the presence of soil suspension. Besides, any small quantity of the acid produced in the first instance would be at once removed from solution and would not be available for hastening the reaction by autocatalysis. All the soils used in this study were made completely base free by exhaustive treatment with 0.05 *N* HCl. Thus all the acetic acid produced by hydrolysis remained in solution, no exchangeable bases being present in soil to react with it.

Before experiments with soils were carried out, it was considered desirable to study the reaction with buffer solutions of known pH value in order to standardize working conditions.

Hydrolysis of ethyl acetate with buffer solutions

To 47.5-cc. portions of the various buffer mixtures (KCl-HCl, acetic acid-acetate; B. D. H. Universal) were added 2.5-cc. portions of ethyl acetate. The mixtures were shaken in a mechanical shaker for 24 hours at room temperature. The acid formed was determined by titrating the original and the final solution. The experiment was repeated at 50°C. in a constant temperature water bath. Shaking (occasional) was done by hand during 4 hours. After this the mixture was at once cooled in ice and titrated as before. The buffer solutions were 0.2 *N* initially in both cases. The results are given in table 1 and in figure 1.

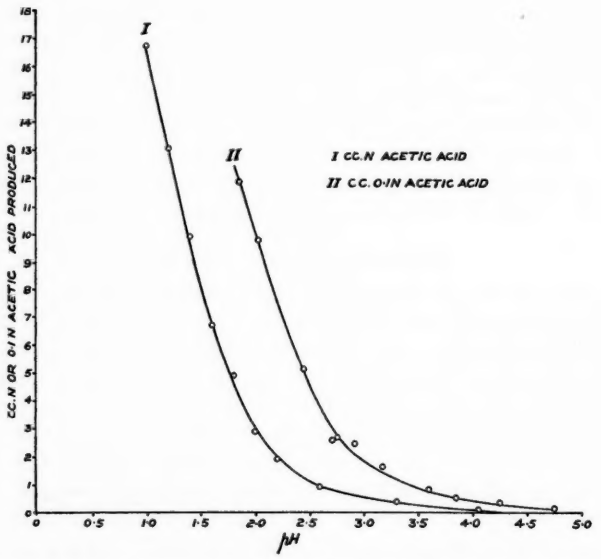

FIG. 1. RELATION BETWEEN pH VALUE AND HYDROLYSIS OF ETHYL ACETATE

It will be seen that the relationship between pH value and hydrolysis of ethyl acetate is capable of being represented by a smooth curve in both cases. It is clear that virtually no hydrolysis occurs above pH 5. If we plot logarithms of the concentration of acetic acid produced against the corresponding pH value, we get straight lines. The relationship is, therefore, capable of being expressed mathematically, and the following formulas are obtained for the two temperatures:

Room temperature, 24 hours' shaking..... $pH = 5 - 1.5 \log_{10} E$
A 50°C..... $pH = 4.6 - 1.2 \log_{10} E$

where E is the amount of acetic acid produced in milliequivalents in both cases.

Effect of the concentration of ethyl acetate solution on hydrolysis

For a study of the effect of the concentration of ethyl acetate solution on hydrolysis, KCl-HCl buffer was used, both the strength of the buffer solution and the concentration of ethyl acetate being varied. The total volume of the buffer and ethyl acetate was 50-cc. in every case. The mixture was kept for 24 hours at room temperature, after which the amount of acetic acid

TABLE 1

Hydrolysis of ethyl acetate with buffer of varying pH value

ROOM TEMPERATURE 24 HOURS		TEMPERATURE 50°C. 4 HOURS	
pH	0.1*N* acetic acid produced	pH	1 *N* acetic acid produced
	cc.		*cc.*
1.86	11.85	1.0	16.725
2.03	9.75	1.2	13.05
2.46	5.10	1.4	9.90
2.59	4.24	1.6	6.70
2.72	2.55	1.8	4.90
2.78	2.62	2.0	2.85
2.93	2.40	2.2	1.90
3.18	1.60	2.59	0.90
3.63	0.80	3.32	0.35
3.87	0.50	4.06	0.05

TABLE 2

Effect of concentration of ethyl acetate and buffer solution on hydrolysis

CONCENTRATION OF BUFFER	pH	CONCENTRATION OF ETHYL ACETATE, PER CENT					
		1	2	4	6	8	10
		0.1 *N* acetic acid produced					
N		*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
2.0	1.85	4.6	9.5	18.9	28.2	36.2	41.5
1.0	2.03	2.15	4.2	8.10	9.75	15.2	17.8
0.4	2.47	0.82	2.04	4.08	6.02	8.66	9.10
0.2	2.73	0.46	1.02	2.03	3.04	4.05	5.06
0.1	3.07	0.26	0.51	1.02	1.62	2.03	....

produced was determined by titrating the original solution and the solution after hydrolysis. The results are given in table 2.

It will be seen from table 2 that the rate of hydrolysis depends on the concentration of ethyl acetate as well as on the concentration of the buffer solution. It must be remembered, however, that the effect of concentration of the buffer is only apparent because dilution affects the pH value of the buffer. The results in tables 1 and 2, if considered on the basis of pH value, are in general agreement. Thus, if we plot logarithms of concentration of acetic acid pro-

duced against pH values, series of straight lines are produced and the relationship can be expressed by the following formulas:

$\text{pH} = 2.5 \log_{10} \frac{C_e}{E}$, where C_e is the concentration of ethyl acetate, expressed in cubic centimeters per 100 cc., and E is the amount of acetic acid produced, expressed in cubic centimeters of 0.1 N solution.

Since $\text{pH} = \log \frac{1}{C_h}$ where C_h is concentration of hydrogen ions, we have

$$\log \frac{1}{C_h} \cdot \frac{E}{C_e} = 2.5$$

or

$$\frac{E}{C_e \cdot C_h} = 10^{2.5}, \text{ i.e., } E = C_e \cdot C_h \times 10^{2.5}$$

which follows from the law of mass action, i.e., hydrolysis is proportional to the product of the active masses, which are the hydrogen ions and ethyl acetate in this case.

It might be pointed out that the maximum solubility of ethyl acetate in water is slightly more than 9 per cent; therefore, the values for 8 and 10 per cent solutions are not very different.

Effect of temperature on hydrolysis of ethyl acetate

A mixture of 47.5 cc. of KCl-HCl buffer of 2.03 pH and 2.5 cc. of ethyl acetate was shaken in a water bath for 1 hour at various temperatures. The results are plotted in figure 2.

It will be seen that temperature plays an important part in the rate of hydrolysis of ethyl-acetate, virtually no hydrolysis occurring at or below a temperature of 10°C.

Hydrolysis with soils

In order to standardize working conditions a number of experiments were performed with one soil, a black cotton soil of high base exchange capacity. It was treated exhaustively with 0.05 N HCl to remove all the exchangeable bases and to convert the clay complex into the acidoid state, followed by leaching with water until the filtrate was free of Cl ions. Two samples, designated P.C. 2 and P.C. 13, from different localities were treated.

The following experiments were carried out with these soils to study the effect of various factors.

Effect of time of contact and the quantity of soil on the hydrolysis of ethyl acetate. Varying amounts of P.C. 2 soil were shaken with 100-cc. of 5 per cent (by volume) solution of ethyl acetate for different lengths of time, after which the suspensions were filtered, and 50-cc. of the filtrate was titrated against standard NaOH, phenolphthalein being used as indicator. The experiment was repeated both at room temperature (23°C.) with 24 hours' shaking, and at 50°C. with 4 hours' shaking. The results are plotted in figure 3, from which it will be seen that the hydrolysis is directly proportional to the amount of

soil. There is a faint indication that the relationship may be exponential, but it is also possible that a very large amount of soil might interfere with the free movement of ethyl acetate, and a slight falling off of the rate of hydrolysis might be expected. It is interesting to note that the pH value of the same soil was determined by the quinhydrone electrode by using soil-water ratios ranging from 1:10 to 7:10. There was absolutely no difference in the pH value, which remained constant at 3.80 irrespective of the soil-water ratio. We have already seen that the change in the rate of hydrolysis in KCl-HCl buffers due to change in concentration of the buffer is entirely ac-

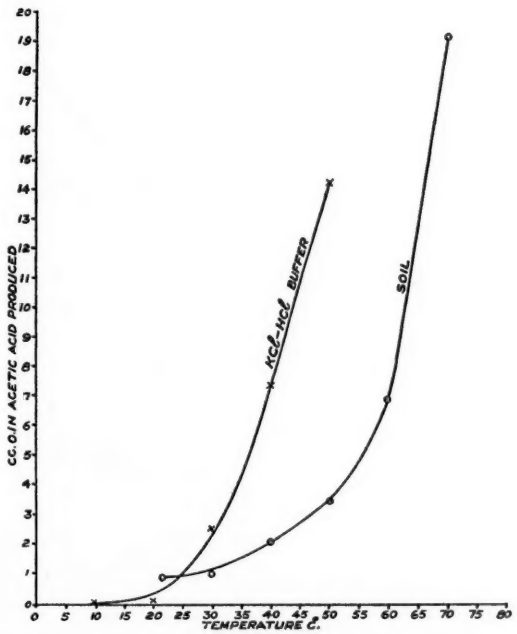

FIG. 2. EFFECT OF TEMPERATURE ON HYDROLYSIS OF ETHYL ACETATE BY SOIL AND KCl-HCl BUFFER AT pH 2.03

counted for by the change in the pH value of the buffer due to dilution (table 2). It is, therefore, evident that the usual electrometric methods of measuring pH values do not give the correct pH value of an acidoid. This conclusion is not surprising when we remember that acidoids are ionized only on the surface and that no hydrogen ions are in true solution.

Effect of concentration of ethyl acetate on its hydrolysis by soil. Fifty cubic centimeters of mixtures of ethyl acetate and water in varying proportions were stirred with different amounts of soil for 4 hours at 50°C., after which they were at once cooled in ice, filtered, and titrated. The results are plotted

in figure 4. It will be seen that hydrolysis is directly proportional to the concentration of ethyl acetate. This conclusion was also reached in the case of buffer solutions.

Effect of temperature on hydrolysis by soils. Ten-gram portions of P.C. 2 soil were shaken for 1 hour with 100-cc. of 5 per cent ethyl acetate solution at different temperatures, and the hydrolysis was measured as usual by titrating the acetic acid in the filtrate. The results are included in figure 2. The results with KCl-HCl buffer of 2.03 pH, in the same graph (fig. 2), indicate

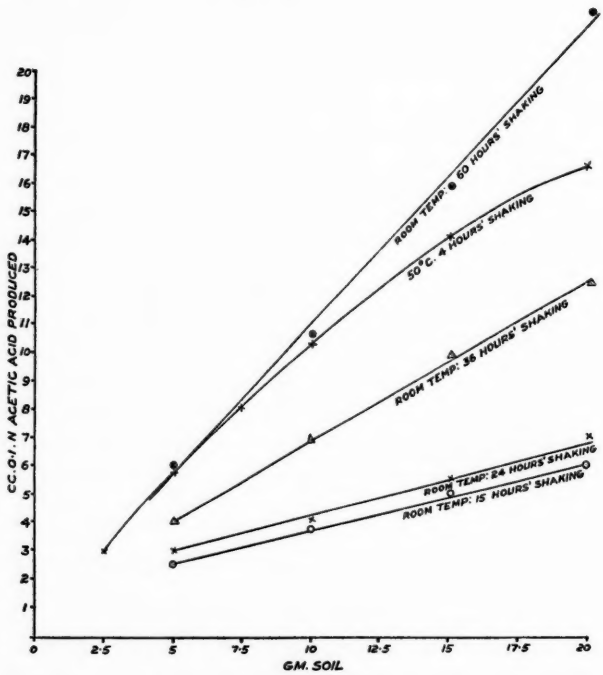
CC. 0·1 N ACETIC ACID PRODUCED
GM. SOIL
ROOM TEMP. 60 HOURS' SHAKING
50°C. 4 HOURS' SHAKING
ROOM TEMP: 36 HOURS' SHAKING
ROOM TEMP: 24 HOURS' SHAKING
ROOM TEMP: 15 HOURS' SHAKING

FIG. 3. EFFECT OF TIME OF SHAKING AND OF QUANTITY OF SOIL ON THE HYDROLYSIS OF ETHYL ACETATE

that the hydrolysis by the buffer solution shows a sudden rise at 25°C., whereas in the hydrolysis by soil, this rise takes place at about 50°C. This is to be expected, as the pH value of the buffer is 2.03 and that of the soil is 3.80. The general shape of both curves, however, is similar and leaves no doubt as to the essential analogy between colloidal acids and true acids.

Hydrolysis of ethyl acetate in alcoholic solutions. Very few measurements of the pH values of alcoholic solutions have been attempted. Alcohol, however, is well known to suppress the ionization of electrolytes. A similar

effect on the surface ionization of acidoids would be expected. This would result in decreased hydrogen-ion activity and consequently in a diminished rate of hydrolysis. Ten-gram portions of P.C. 2 soil were shaken with 50-cc. of 5 per cent alcoholic solutions of ethyl acetate containing varying amounts of alcohol. The results are given in table 3. It will be seen that alcohol decreases the hydrolysis to a marked extent. This is in agreement with its known effect on other electrolytes, in suppressing their dissociation. The dissociation of acidoids, therefore, is of the same type as the dissociation of true electrolytes.

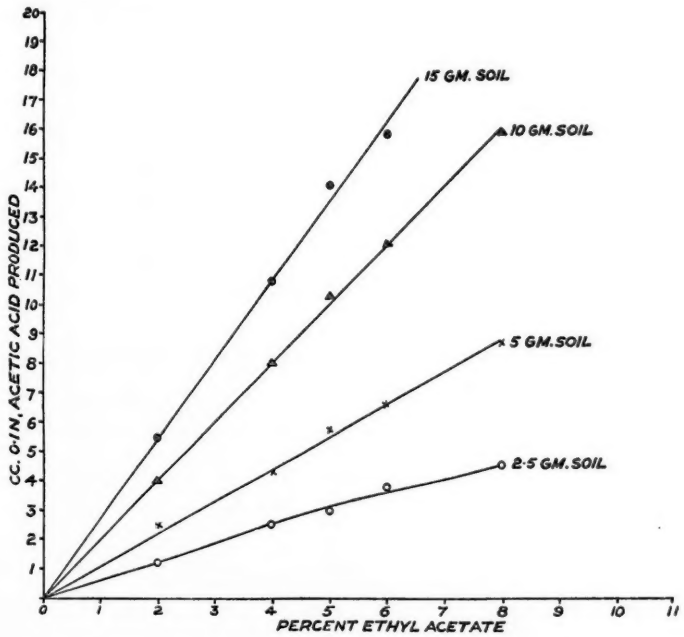

FIG. 4. EFFECT OF CONCENTRATION OF ETHYL ACETATE ON HYDROLYSIS BY SOIL

Effect of gradual neutralization of the soil acidoid on the hydrolysis of ethyl acetate. P.C. 13 soil was neutralized with NaOH by the addition of increasing amounts of the alkali to 10-gm. portions of soil. Sufficient water and ethyl acetate were added to give 50-cc. of 5 per cent solution in every case. The mixtures were kept at 50°C. for 4 hours with frequent shaking by hand. After this, they were cooled and filtered, and an aliquot of the filtrate was titrated as usual to determine the acetic acid formed. The results are given in table 4. It will be seen that the first lot of alkali produces a great change in the hydrolyzing power, after which the change becomes more gradual until the

hydrolyzing power is completely destroyed. Because of the limited range for soils in which hydrolysis is possible, as hydrolysis ceases altogether at pH values above 5.35, the method is not suitable for finding the titration curves of soils. The results are interesting, however, in establishing the analogy between acidoids and true acids.

HYDROLYSIS OF ETHYL ACETATE WITH DIFFERENT SOILS

The working conditions having been standardized, it appeared of interest to determine the pH value of acidoids from different soils. Forty-two soils from different places were examined in this connection.[1] They were treated

TABLE 3

Hydrolysis of ethyl acetate in alcoholic solutions

ALCOHOL	0.1 *N* ACETIC ACID PRODUCED
per cent	*cc.*
0	4.25
85	1.6
90	1.5
95	1.4
100 (absolute)	0.9

TABLE 4

Hydrolysis of ethyl acetate by P.C. 13 soil gradually neutralized with NaOH

0.1 *N* NaOH ADDED TO 10 GM. OF SOIL	pH	0.1 *N* ACETIC ACID PRODUCED IN 50 CC.
cc.		*cc.*
0	3.49	10.25
10	4.45	5.00
20	4.85	3.50
30	5.35	2.00
40	6.25	0.0
50	7.50	0.0

first with 0.05 *N* HCl until free from exchangeable bases and then with water until free from Cl ions. A final washing with alcohol was given to facilitate drying and powdering.

Ten-gram portions of the treated soil were shaken with 50-cc. of 5 per cent ethyl acetate solution for 4 hours at 50°C. Shaking was done by hand at frequent intervals, after which the mixture was cooled and filtrated, and an aliquot was titrated with standard alkali. From the quantity of acetic acid produced, the pH value was interpolated from figure 1. The pH value of the original soil as well as the pH values of the treated soils were determined

[1] These soils were from Professor Mitscherlich's collection which he had used for experiments on manurial requirements.

TABLE 5

Inversion of sucrose and hydrolysis of ethyl acetate by various soils, together with other constants

SERIAL NUMBER	CLAY	pH OF ORIGINAL SOIL	pH OF ACID-TREATED SOIL			DISPLACED ACID BY KCL, PER 100 GM. SOIL				TITRATION TO pH 5, ALKALI PER 100 GM. SOIL	HYDROLYSIS, ACID	SUGAR INVERSION
						Single treatment		Leaching				
			Direct	Hydrolysis	Sugar inversion	Phenolphthalein	Methyl orange	Phenolphthalein	Methyl orange			
	per cent					*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*gm.*
1	32.2	7.32	3.18	3.24	3.28	12.0	4.0	15.5	5.3	15.0	0.4	0.5048
2	13.8	7.49	3.77	3.75	....	6.0	0.8	8.0	1.5	3.75	0.15	.....
3	20.6	7.64	3.67	3.80	3.96	5.6	0.8	8.9	2.0	5.0	0.125	0.0850
4	8.7	7.64	3.67	3.75	4.06	4.0	0.8	6.7	1.3	3.75	0.15	0.1050
5	11.5	7.92	3.67	3.55	3.52	8.8	2.4	11.6	3.0	4.5	0.225	0.225
6	16.0	8.14	4.29	3.80	3.82	4.0	...	6.3	0.2	2.0	0.125	0.120
7	13.9	7.90	3.57	3.68	3.54	5.6	1.2	8.2	2.0	5.5	0.175	0.200
8	29.8	7.50	3.08	3.22	3.28	11.6	4.4	13.5	4.1	12.0	0.41	0.4875
9	9.3	7.61	3.42	3.68	4.02	5.2	0.4	7.0	1.1	3.5	0.175	0.075
10	25.3	6.94	3.44	3.22	3.42	10.0	2.6	11.4	2.2	10.2	0.325	0.325
11	19.1	7.52	3.80	3.68	3.58	5.84	1.2	9.32	1.9	2.37	0.175	0.195
12	18.3	6.84	3.31	3.55	3.52	6.56	2.0	6.7	3.2	2.90	0.225	0.230
13	9.0	7.30	4.23	4.02	4.23	2.8	...	4.9	0.2	0.5	0.6	0.0475
14	15.8	7.56	3.38	3.58	3.66	6.0	1.6	6.5	2.8	1.62	0.2125	0.165
15	25.7	7.74	3.38	3.40	3.45	9.2	3.2	11.0	3.0	4.5	0.3	0.287
16	5.8	7.78	3.77	3.80	3.91	3.6	0.4	5.5	1.0	0.89	0.125	0.95
17	14.6	6.68	3.98	3.88	4.00	3.2	...	5.6	0.6	1.12	0.100	0.80
18	33.3	5.60	3.84	3.80	3.72	4.8	1.2	6.8	1.3	1.62	0.125	0.145
19	27.8	5.92	3.83	3.75	3.64	6.8	1.6	9.2	2.1	2.12	0.15	0.175
20	20.7	7.54	4.07	3.95	3.94	3.6	...	5.2	0.1	1.0	0.075	0.090
21	8.9	7.76	....	....	....	7.1	3.8	10.2	5.1	.....	0.633	0.300
22	2.3	7.84	3.54	3.75	3.78	3.4	1.0	5.3	1.6	1.62	0.15	0.130
23	16.4	7.98	3.77	3.88	3.72	4.8	1.4	6.3	1.7	1.25	0.10	0.146
24	8.9	7.51	4.06	3.95	4.00	3.2	0.2	4.1	0.3	0.75	0.075	0.080
25	15.4	8.00	3.44	3.50	3.57	6.2	2.0	7.4	2.6	3.25	0.25	0.200
26	19.6	7.70	3.44	3.70	5.58	5.6	1.6	7.2	2.3	2.12	0.165	0.195
28	11.9	7.16	4.23	3.95	4.06	3.4	0.4	4.7	0.6	0.89	0.075	0.070
29	10.9	7.66	4.13	3.54	3.90	4.0	0.4	5.1	0.7	1.12	0.238	0.10
30	18.8	6.96	3.42	3.75	3.90	5.8	2.0	7.2	2.4	1.89	0.15	0.10
31	8.3	6.52	3.87	4.04	4.10	2.4	0	3.3	0	0.75	0.05	0.065
32	22.9	6.96	3.38	3.68	3.38	7.2	2.6	9.4	3.3	2.89	0.175	0.37
33	16.0	7.64	4.10	3.95	3.80	3.2	0.8	5.0	1.3	0.75	0.075	0.12
34	6.9	5.08	4.49	4.06	4.18	2.6	0.6	4.3	0.7	0.5	0.15	0.055
35	22.8	5.23	3.67	3.75	3.78	5.0	1.6	6.5	1.7	1.5	0.15	0.130
36	5.4	5.18	4.49	4.0	4.30	2.4	0.2	3.4	0.3	0.5	0.0625	0.040
37	8.0	6.62	3.20	3.62	3.57	4.0	1.2	5.5	1.6	2.12	0.188	0.225
38	9.6	7.56	3.80	3.80	3.60	3.8	1.0	5.4	1.2	0.89	0.125	0.185
39	12.8	7.12	3.41	3.80	3.54	3.6	0.8	4.9	1.0	1.25	0.125	0.215
40	47.0	5.16	3.64	3.80	3.59	3.0	0.6	5.7	1.3	3.75	0.125	0.190
41	48.3	5.76	4.58	3.82	3.78	4.0	0.4	5.8	0.8	0.75	0.125	0.130
42	19.1	5.68	3.74	3.80	3.50	6.2	2.0	7.9	2.3	1.5	0.125	0.235
P.C. 1	11.3	8.48	4.26	3.62	3.92	3.2	0.4	4.4	0.4	0.45	0.2	0.095
P.C. 2	59.3	8.23	3.84	3.40	....	35.2	5.0	36.9	5.6	5.5	0.3	0.700
P.C. 3	62.2	7.56	3.25	2.62	....	28.6	4.0	31.1	4.3	19.5	0.85	0.950
P.C. 7	21.8	9.59	5.31	4.22	4.36	2.2	0.2	3.1	0.3	0.0	0.25	0.035
P.C. 13	58.9	8.57	3.49	2.60	....	27.8	10.0	31.1	12.5	12.2	0.025	1.5169
P.C. 15	22.4	7.85	4.66	4.06	4.10	2.8	0.4	3.9	0.4	0.2	0.05	0.065
						S_p	S_m	L_p	L_m	T	H	I

with the quinhydrone electrode. The treated soils were also shaken with *N* KCl solution, and the total acid produced in a single shaking, as well as after leaching with KCl, was also determined. The results are given in table 5.

It will be seen that the agreement between the pH values determined directly and those found by hydrolysis is good. When the inherent errors in the measurement of pH value of soils by the electrical as well as by the hydrolysis method are considered, the agreement must be reckoned as very close.

The titration curves of the treated soils were determined with the quinhydrone electrode, NaOH being used to neutralize the soils. The object was to see whether there was any correlation between the amount of alkali required to bring the soil to pH 5 and its hydrolyzing power. A good correlation was expected, as all hydrolysis ceases at pH 5. One gram of soil was left for 24 hours in 5 cc. of NaOH solution of increasing concentration. The pH values were then determined with the quinhydrone electrode. From the titration curves thus obtained the alkali required to bring the soil to pH 5 was interpolated. These interpolated values are included in table 5. It is well known that neutral salts, on coming into contact with acidoids, bring into solution true acids, together with some aluminum and iron. Opinion differs as to the mechanism of this aluminum dissolution. Some regard it as the result of replacement from the soil; others consider it a produce of secondary reactions between the acid produced and the clay complex. Al and Fe brought into solution behave like acids. They are, however, distinguished from the true acids by titration with alkali, methyl orange being used as indicator. If the titrations are conducted in the presence of phenolphthalein, Al and Fe appear as acid. It was of interest to determine the relation between the acid produced by the replacement with a neutral salt and the hydrolyzing power of the soil. Ten-gram portions of the acid-treated soils were taken with 200 cc. *N* KCl solution for 2 hours and filtered. An aliquot of the filtrate was titrated with standard alkali, phenolphthalein being used as indicator. Another aliquot was titrated with the same alkali, methyl orange being used as indicator. The soil was then leached with 500 cc. *N* KCl in 100-cc. lots. The combined filtrates were made up to a definite volume, and aliquotes were titrated to phenolphthalein as well as to methyl orange. The results are included in table 5.

The following correlations were worked out between hydrolysis in milliequivalents of acid produced (H) and (S_p) displaced acid with KCl single treatment, titrations to phenolphthalein; (S_m) same as (S_p) but titrations to methyl orange; (L_p) displaced acid by leaching with KCl solution, titrations to phenolphthalein; (L_m) same as (L_p) but titrations to methyl orange; (T) titration of soil to pH 5 with NaOH (all quantities expressed in milliequivalents per 100-gm. of soil):

	(S_p)	(S_m)	(L_p)	(L_m)	(T)
(H).....	0.69	0.77	0.59	0.77	0.82

It will be seen that correlation is best between T and H, that is, titration value to pH 5 and the hydrolysis of ethyl acetate. The correlation between H and displaced acid is better when titration is done with methyl orange than with phenolphthalein. This will be readily understood from the fact that both hydrolysis and inversion become inappreciable above pH 5. The acid displaced above this pH value, therefore, will not be correlated. It must be pointed out that a correlation between intensity and capacity is not strictly justified, because we know that pH and exchangeable bases cannot be correlated; however, in the case of completely unsaturated soils a correlation between quantity and intensity might be expected, provided the dissociation constants of colloidal acids in different soils were close to one another. The validity of this assumption is confirmed by the significance of the correlation.

SUGAR INVERSION

Inversion of sucrose by soil has been studied by Hanley (3) and more critically by Rice and Osugi (7), who showed that a suspension of soil inverts several times as much sugar as does an extract of the same soil. The experimental technic employed by these workers left much to be desired. This was pointed out by the senior author in an earlier publication (6), in which some preliminary results were given.

In ordinary circumstances, with mineral acids, the polarimetric method of determining inversion of sucrose is the best. Difficulties are experienced, however, in the use of the polarimetric method with soils: first, it is difficult to obtain a clear solution in many cases; secondly, the actual inversion is very small as compared to the total concentration of the sugar solution, and consequently only a very small change occurs in the polarimetric reading, which is already very high. Titration of Fehling solution was free from these objections and was successfully used in this case.

Standard Fehling solutions were made (*a*) by dissolving 69.28 gm. of $CuSO_4$(A.R.) to 1 liter, (*b*) by dissolving 350 gm. of Rochelle salt (sodium potassium tartrate) and 120 gm. of pure NaOH and making up to 1 liter. Five cubic centimeters each of the two solutions were mixed, diluted with about 30-cc. of water, and gently boiled. The boiling solution was titrated with the sugar solution, care being taken that the glucose in the solution did not exceed 1 per cent. Near the end point, which was determined by a preliminary rough titration, two drops of 10 per cent methylene blue were added. Every time the Fehling solution was used, it was standardized with freshly prepared 1 per cent glucose solution.

As both glucose and fructose formed by inversion, better known as invert sugar, are capable of reducing Fehling solution, it was always the total invert sugar solution that was determined. A blank reading with sugar solution used was also taken every time to allow for the glucose in it.

Relation between pH value and sugar inversion

Acetate-acetic acid buffers of different pH values were used in the study of the relation between pH value and sugar inversion. The results are plotted in figure 5. It will be seen that the general shape of the curve is similar to that expressing the hydrolysis of ethyl acetate in terms of pH value, and the relation is defined by the following formula:

$$pH = 2.3 - \log_{10} E$$

when E is the sugar inversion in grams per 25-cc.

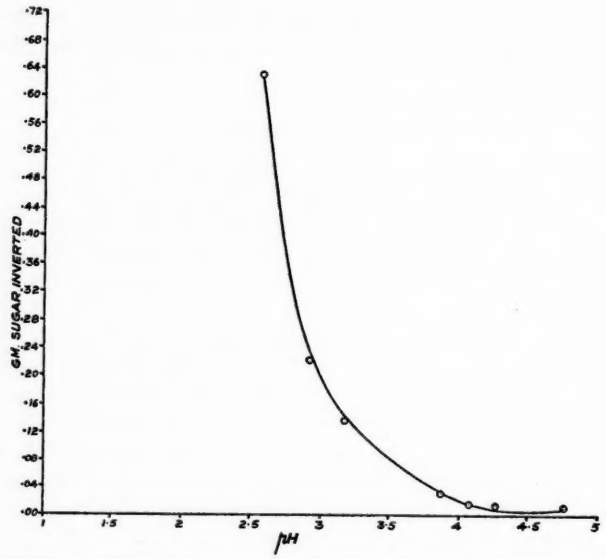

FIG. 5. RELATION BETWEEN pH VALUES AND SUGAR INVERSION Na-ACETATE-ACETIC ACID BUFFER, 4 HOURS' SHAKING AT 60°C.

Effect of time and concentration of sugar on inversion by soil

Inversion of sugar was studied by taking 2.5 gm. of P.C. 2 soil and 25-cc. of sugar solution of varying concentration. The mixtures were kept in a water bath at 40°C. for periods of times ranging from 15 minutes to 4 hours. After that the bottles were immediately cooled in ice water and filtered. Ten cubic centimeters of the filtrate was added to 10-cc. of the Fehling solution. Reduction of the Fehling solution was completed with standard glucose solution. The decrease in the quantity of glucose solution from that required for the original Fehling solution was equivalent to the invert sugar in the unknown sugar solution. The inversion was, thus, known in terms of a standard solution of glucose. The results are given in table 6.

It will be seen that inversion of sugar, like the hydrolysis of ethyl acetate, depends on the concentration of sugar and the time of contact.

TABLE 6

Effect of time and concentration of sugar on its inversion by soil (P.C. 2)

TIME OF CONTACT	INVERT SUGAR IN 25 CC. AT VARIOUS CONCENTRATIONS OF SUGAR SOLUTION				
	2 per cent	8 per cent	12 per cent	16 per cent	20 per cent
hours	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0.25	0.0075	0.01	0.01125	0.0175	0.015
0.5	0.01	.....	0.01875	0.0200	0.0225
1.0	0.015	0.0225	0.02625	0.0275	0.0325
2.0	0.0175	0.0275	0.03375	0.035	0.0425
3.0	0.0175	0.235	0.04125	0.050	0.055
4.0	0.020	0.040	0.04625	0.60	0.065
5.0	0.020	.....	.....	.....	.....

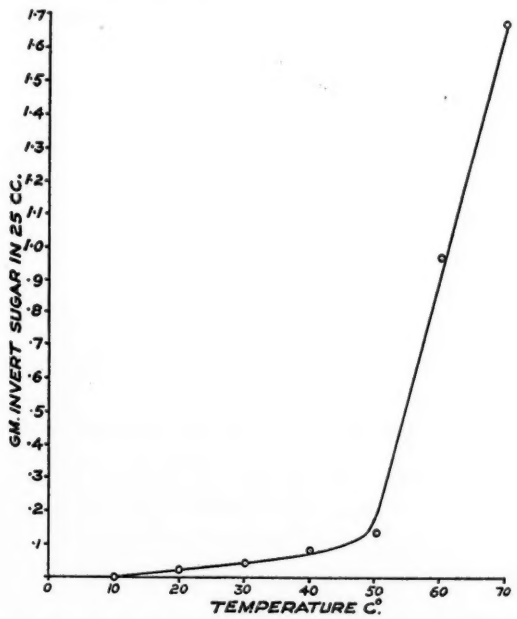

FIG. 6. EFFECT OF TEMPERATURE ON INVERSION BY P.C. 13 SOIL

Effect of temperature on inversion

To 2.5-gm. portions of P. C. 13 soil in bottles was added 25-cc. of 20 per cent sugar solution. The bottles were kept at different temperatures for 4 hours, being shaken occasionally by hand. The results are plotted in figure

6. It is seen that an abrupt rise occurs in the rate of inversion above 50°C. It appears that the rate of inversion is very slow below 50°C. and that to produce measureable effects the temperature should be about 60°C. The necessity of controlling the temperature in this region is also apparent from the steepness of the curve.

Effect of quantity of soil on inversion

To quantities of P.C. 13 soil, ranging from 1.25-gm. to 15-gm., were added 25-cc. portions of 20 per cent sugar solution. The mixtures were kept at 60°C. for 4 hours, being occasionally stirred by hand, after which they were

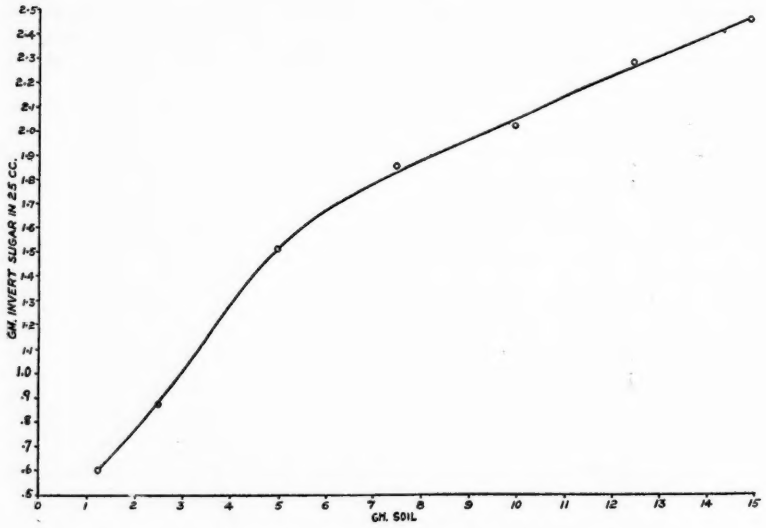

FIG. 7. RELATION BETWEEN QUANTITY OF SOIL AND INVERSION OF SUGAR

cooled in ice and filtered. The filtrate was examined for inversion. The result, plotted in figure 7, show that inversion is proportional to the quantity of soil.

Inversion of sugar with various soils

The same series of soils used for hydrolysis of ethyl acetate were employed for sugar inversion. Five grams of each soil was kept in contact with 25-cc. of 20 per cent sugar solution at 60°C. for 4 hours.

The pH values of the soils, interpolated from the curve for buffer solutions (fig. 5), were found to be generally lower by 0.6 than those determined by hydrolysis. To obtain pH values of soils comparable with the pH values found by hydrolysis of ethyl acetate, therefore, 0.6 should be added to the

interpolated values. It is a remarkable fact that this lowering of the pH value corresponds with the observations of Moran and Lewis (4) and of Corran and Lewis (1, 2) that sucrose possesses the property of causing a large increase in the activity of various ions while not appreciably altering their concentration. These results are of great importance insofar as they bring the hydrion activity of acidoids into line with that of true acids. The results of sugar inversion and the corrected pH values are included in table 5 and show a good agreement with the values obtained by hydrolysis.

Correlation of values for sugar inversion (I) with those for displaced acid by KCl, both by single treatment and by leaching, as well as with those for alkali titer to pH 5 were worked out as for hydrolysis of ethyl acetate. The correlation coefficients were as follows:

	(S_p)	(S_m)	(L_p)	(L_m)	(T)
(I)	0.73	0.74	0.62	0.75	0.71

These correlations run parallel to similar correlations worked out for hydrolysis, though they show less variation.

TABLE 7

Inversion of sugar with P.C. 13 soil gradually neutralized with NaOH

0.1 *N* ALKALI PER 10 GM. OF SOIL	pH	INVERT SUGAR
cc.		*gm.*
0	3.49	1.542
4	4.05	1.388
10	4.45	1.041
20	4.85	0.625
40	6.25	0.034
60	9.15	.....

Titration curve of soil by sugar inversion

Five-gram portions of P.C. 13 soil were added to 25-cc. of 20 per cent sugar solution containing different amounts of NaOH. The mixture was kept at 60°C. for 4 hours, and the amount of invert sugar was determined as usual by cooling, filtering, and titrating with Fehling. The results are given in table 7.

A comparison between tables 4 and 7 shows that hydrolysis ceases at a lower pH value than that at which inversion ceases. The shape of the curves showing the relation between pH and hydrolysis as well as the relation between pH and sugar inversion does not admit of extrapolation, but it is clear from those curves that hydrolysis of ethyl acetate becomes inappreciable between 4.5 and 5, whereas inversion stops somewhere about pH 5.5. It is worthy of note that both sugar inversion and hydrolysis continue to take place up to a higher pH value in the case of soils than in the case of buffer solutions. The fact emphasizes the unreliability of the usual electrical methods of measuring soil reaction.

SUMMARY

Hydrolysis of ethyl acetate and inversion of sucrose were studied with soil acidoids. The general analogy between colloidal acid (acidoids) and true acids has been brought out by a comparison of the catalytic activity of hydrogen ions in both cases.

REFERENCES

(1) CORRAN, J. W. 1923 Effect of sucrose on activity of certain ions. *Jour. Amer. Chem. Soc.* 45: 1627.

(2) CORRAN, J. W., AND LEWIS, W. C. M. 1922 The effect of sucrose on the activities of the chloride and hydrogen ions. *Jour. Amer. Chem. Soc.* 44: 1673.

(3) HANLEY, J. A. 1914 The humus of acid and alkaline peats. *Jour. Agr. Sci.* 6: 63.

(4) MORAN, T., AND LEWIS, W. C. M. 1922 Studies in catalysis. XVI. The inversion of sucrose by hydrogen ions. *Jour. Chem. Soc.* 121: 1613–1624.

(5) PARKER, F. W., AND BRYAN, O. C. 1923 Soil acidity as measured by sugar inversion, the Truog test and the hydrogen-ion concentration and its relation to hydrolysis of ethyl acetate. *Soil Sci.* 15: 99–107.

(6) PURI, A. N. 1930 Studies in soil colloids. I. Base exchange and soil acidity. *Mem. Dept. Agr. India, Chem. Ser.* 9 (I): 1–38.

(7) RICE, F. E., AND OSUGI, S. 1918 The inversion of cane sugar by soils and allied substances and the nature of soil acidity. *Soil Sci.* 5: 333–358.

ON THE FORMATION OF STRUCTURE IN SOIL: IV. THE STRUCTURE OF MIXED CLAY-SAND AND CLAY-HUMUS FORMATIONS

D. I. SIDERI

Agricultural Institute, Voronezh, U. S. S. R.

Received for publication March 24, 1938

Numerous studies, based on ideas advanced by Gedroiz, regarded the formation of soil structure as a process of simple coagulation of soil colloids under the action of calcium. These studies did not take sufficiently into account the physical conditions of structure formation and the possibility of an orientation of primary elements in the formation of the structural aggregate. Many phenomena of some importance to the understanding of the properties of soil remained unexplained. Examples may be cited which raise doubt as to the correctness of the value attributed to the rôle of absorbed calcium in the formation of watertight structure (1, 8, 11, 15, 21). On the other hand, instances are well known of the failure of a great amount of organic matter, even in the form of slightly soluble calcium humate or aluminum and iron humates, to give rise to a watertight structure in soil (6, 21). To explain these phenomena it proved necessary to resort to various hypotheses, such as that structure formation "is mainly due to humine substances, freshly precipitated under the action of calcium" (25), or that that part of organic matter in soil which is comparatively inert, both biologically and biochemically, is the factor of structure formation (14). To the same class of but weakly grounded hypotheses belongs also that of "active humus" (17). "Active humus" is anything but active in the formation of a watertight structure. The works of Heltzer (8) have established the fact that a watertight structure is formed by an insignificant quantity of organic substance, arising in soil as the result of the process of humus mineralization. Thus we are brought to the necessity of revising our ideas of soil, and our first step in this direction must consist in studying the interactions of the components of soil.

ON THE NATURE OF MIXED FORMATIONS

There is no need to enumerate the older investigations on the solvent action of humus substances on various minerals and rocks. It need only be remarked that these studies produced no generalizations capable of practical application. Certain individual observations, however, are of interest. They produce evidence that mineral-humus compounds of a continuously changing composition are actually forming. Such compounds were termed "mutable" (3), but, unfortunately, their nature was not explained.

At the present time, with the development of colloid-chemical ideas in their application to soil science, soil colloids are considered as salts of the silicic and humine acids with strong bases or with iron and aluminum hydrates (9). But, as has been noted, neither calcium humates nor humates of trivalent metals produce a watertight granular structure. We must, therefore, turn our attention to phenomena of another, but little investigated, order and seek for explanations of structural properties in the study of the nature of the union of particles of heterogeneous composition and size. The chief observation by which one must be guided in this case, is that the components of soil—sand, clay, humus, oxides—rarely, if ever, are found isolated in soil. The soil-forming process determines the distribution of these components and their mutual orientation. No special studies of this problem have been made. The literature contains only a few references to the possibility of heterogeneous formations, based mainly on the consideration of active colloidal material as an amorphous jellylike mass enveloping solid mineral grains (2, 6). Some authors have thought that these colloidal envelopes lend the soil a cell structure (6, 7). Still earlier, however, Schloesing (13), on the basis of his observations, pointed out the specific rôle of the components of soil in the process of structure formation. He attached great importance to such complexes as clay-sand and clay-humus, in the belief that clay cements sand and that humus cements clay. The author has taken these works of Schloesing as the starting point for further investigations on soil structure.

In his preceding report (15), the author established the existence of a very firm bond between clay and quartz sand. This phenomenon was explained on the basis of the fact that the mixture of clay with sand is subject to the law of mutual orientation based on the similarity of crystalline periods. Besides this kind of bond, an interaction of another order exists between particles of clay and sand. Observation shows that in this case a laminated system is formed, possessing anisotropic properties only when the amount of sand is below a certain limit. Only under such a condition is a structure formed whereby groups of parallel anisotropic clay particles serve as centers of crystallization. Under the microscope one can see the grains of sand uniting with these parallel laminas of clay. The resulting structure of the mixture does not differ from the structure of pure clay. If the amount of sand in the mixture is increased, however, structure disappears, and a clear-cut separation appears between the two components of the mixture.

The phenomenon described can be readily observed under the microscope if the preparation is made as follows: A small quantity of swollen Na-clay gel is placed on a glass slide, and on one side at the very edge of the preparation a little fine quartz sand (0.01–0.02 mm.) is added. If a cover slip is cautiously placed on this preparation, a mixture is obtained in which the concentration of sand gradually decreases toward the opposite edge of the preparation. It is possible to observe under the microscope how the structure disappears in the mixture with a higher content of sand (pl. 4, fig. 1, lower part) and how,

as the sand content decreases, the grains of sand begin to unite with the clay particles, until, at a certain ratio of sand to clay, the structure of the mixture is similar to that of clay (pl. 4, fig. 1, upper part).

The phenomena of structure formation in mixtures of clay and sand, as described, explain the weakening and disappearance of the granular structure in chernozem when this soil is mixed with sand. Such a gradual weakening of structure under the influence of the admixture of sand was observed by Nabokikh in the southern steppes of Ukraine, lying close to the sand dunes of the left banks of steppe rivers (12).

The question of the bond between humus and clay is of no less interest than that of the bond between sand and clay. It is to be expected that the elucidation of the nature of these mixed formations will supply information on the origin of the compact granular structure of chernozem, on the process of its formation, and on the symptoms accompanying its destruction. In our preceding work (15) it was found that clay possesses the ability to bind humus irreversibly, but no typical characteristics for the differentiation of mixtures with a higher or lower humus content by means of microscopic examination were found. Dendritic structure, together with the spheroliths of the monaxial crystal, appeared but rarely.

As original material, we used colloidal Na-clays, as in our earlier experiments, and also rocks containing almost pure kaolinite and bentonite. In preparing the mixtures, Na-humate, isolated from peat, and a water-soluble humate, obtained by decomposing manure, were used. Both kinds of humates were thoroughly purified by dialysis. A study of the X-ray spectra of these humates showed the absence of crystalline substances.

The investigation of the mixtures showed that clay and humus mix in any ratio but that no chemical compound seems to be formed. The formation of the mixture, insofar as one may judge from microscopic analysis, takes place in the following manner. Anisotropic colloidal particles of clay act on the isotropic particles of humus in such a way that the latter become anisotropic and assume the state of equilibrium corresponding to their anisotropic condition. Lamina of the clay substance serve as centers of crystallization, and the ability of humus to crystallize is determined by the number of such centers. If the amount of humus does not exceed the number of centers of crystallization, the structure of the mixture seems perfectly homogeneous and makes up an integral mass, differing in no way from the structure of pure clay. Thus, clay is the substance governing crystallization. If the amount of humus exceeds the number of centers of crystallization, the excess humus assumes the state of equilibrium which corresponds to its isotropic condition. A segregation of the mixture, corresponding to the different states of equilibrium, takes place. Isotropic humus, having a high surface tension, must distribute itself on the periphery of the mixed clay-humus formation, and the more viscous crystalline component substance of the mixture will occupy a central position. In liquid mixtures containing a great excess of humus, the state of

equilibrium corresponding to the isotropic condition of humus prevails, as a result of which double refraction disappears.

Evidence that the phenomena described actually take place may be obtained both with the aid of physicochemical methods of studying mixed clay-humus formations and with that of X-ray or microscopic investigation.

Humus, crystallizing on clay, forms a kind of pseudomorphosis and thus is in the closest possible contact with the particles of clay. This contact leads to a lowering of solubility as the result of the compression of the ion envelope around the particles. It is evident, from my observations, described in a preceding report (15), and from the experiments of Tyulin (19, 20), that a relatively large amount of humus is firmly held by clay even when this is subjected to hydrolysis with strong alkali. Another observation, consistent with that of the lowering of the solubility of humus held by clay, is that the absorption capacity of gels containing firmly held organic matter decreases abruptly in comparison with that of the free fraction of humates (20). Other experiments of Tyulin show that the elimination of humus by oxidation with hydrogen peroxide gave rise to an increasing exchange capacity of the clay to which the humus had been firmly held. A similar phenomenon of the increase of exchange capacity after H_2O_2 treatment was observed by Meyers for Hays-colloid, isolated from chernozem (11).

In addition to the mixtures prepared from pure kaolinite or bentonite and humus, samples of gels isolated from soil at the Suma Agricultural Experimental Station by the method of fractional peptization were also subjected to X-ray analysis (16). These gel samples differed in regard to the firmness of their bond with humus, and their clay content ranged from 13.2 to 85.4 per cent. In every case, both in artificially prepared mixtures and in gel samples isolated from soil, the spectra obtained proved to be those of the clay component. This shows that we are dealing here with a nonhomogeneous formation, composed of two homogeneous parts united and mutually oriented in a definite manner. Microscopic study shows that the mixture is composed of clay laminas, surrounded by humus laminas of the same shape as those of clay. The structure of the mixture, therefore, is no different from that of pure clay (pl. 4, fig. 2).

THE INFLUENCE OF AN ADMIXTURE OF IRON AND ALUMINUM HYDROXIDES ON THE BINDING OF HUMUS BY CLAY

Anisotropic colloidal particles of clay when covered with the water films are arranged parallel to one another, forming a doubly refracting system. The formation of one crystal from these particles, each of which forms a continuation of the space lattice of the other, is hindered by admixtures. The purer the clay, the thinner are the laminas of these contaminations. Since the usual contaminations of clay are iron and aluminum hydroxides, it becomes necessary to study the influence of these oxides on the binding of humus. As α-$Fe_2O_3 \cdot H_2O$ (göthite) and α-$Al_2O_3 \cdot 3H_2O$ (bayerite) were used for these

experiments, it was necessary, first, to establish whether they are able to form aggregate anisotropic structures and whether they possess an orienting influence on humus. Observation under the microscope shows that neither of these hydroxides forms anisotropic structures. Mixture of these oxides with humus produces a confused coagulation. It is to be expected, therefore, that with the increase of admixed sesquioxides, not only will the inherent ability of clay particles to aggregate be lowered, but the orienting influence of clay on humus particles as well. Indeed, observation shows that an increased quantity of iron in colloidal clay lowers the ability of clay to form a structure and to orient humus.

For use in the study of the influence of oxide admixtures, samples were prepared, the chief component of which was kaolinite. Schneeberg (Saxony) kaolin, which was shown by X-ray analysis to be almost pure kaolinite, was chosen for this study. Kaolin was first saturated with Na ions and then thoroughly purified by dialysis. The following materials were utilized as hydroxides for the preparation of mixtures:

Bayerite—α-$Al_2O_3 \cdot 3H_2O$, a metastable trihydrate, obtained, by the method of Fricke and Meyring (4), by passing CO_2 into an alkaline solution of aluminate. The precipitate was washed with distilled water and then thoroughly purified by dialysis. The X-ray spectrum of this hydroxide coincided perfectly with the Weiser and Milligan diagram (23).

α-Fe_2O_3—stable iron oxide, of a red-brown color, obtained by slowly heating a 0.33 *M* solution of $FeCl_3$ to 90°C., washing it subsequently with water and then with dilute ammonium hydroxide. The precipitate thus obtained was purified by dialysis. The X-ray pattern corresponded to that of the oxide α-Fe_2O_3 (24).

The clay-hydroxide mixtures were prepared in the following manner. Varying quantities of one or both of the hydroxides were added to a definite amount of kaolinite and thoroughly mixed. After the resultant mixtures had become homogeneous, equal quantities of Na-humate were added to each. After the addition of humus, mixing was again carried out and was continued until the mixture became too dry to allow further mixing. This method was used in order to prevent concentration of the humate at the surface of the material as a result of the high surface tension. The mixture was then air dried, and 5-gm. samples, on the dry basis, were taken. These were treated with water in order to isolate the suspensions. The quantity of the suspension isolated was not determined. After the suspension was precipitated with a 2 per cent solution of KCl and washed with a 1 per cent solution of the same salt, the carbon content was determined. The kaolin remaining after the isolation of the suspension, was thoroughly washed with water, and its carbon content, likewise, was determined. The composition of the oxides admixed to kaolin and the amount of carbon firmly bound to the material of the mixture are shown in table 11. The conclusion that the oxides have a positive influence on the binding of humus is applicable only to the admixture of insignificant

amounts of iron and aluminum oxides. Only in this case do anisotropic clay particles have an orienting influence on both the particles of oxides and those of humus. This influence, however, does not extend above a 1 to 2 per cent content of oxides. Increased contents of oxides cause disorientation, and a phenomenon of the same order is observed as that in mixtures of sand with clay and of clay with humus. The binding of humus, observed in mixtures with a higher oxide content, is explained by the flocculation of humus by hydroxides and not by the orienting influence of kaolin.

Microscopic studies of these mixtures confirm the foregoing conclusion. When the quantity of sesquioxides is increased, the anisotropic colloidal particles of kaolinite lose their ability to distribute themselves in parallel rows. This orienting capacity is preserved, however, when the quantity of oxides is insignificant. Microscopic study has shown that with an excess of sesquioxides,

TABLE 11

Composition and carbon content per gram of kaolin-oxide mixtures

COMPOSITION OF MIXTURE	CARBON	
	In kaolin remaining after isolation of suspension	In suspension isolated from kaolin
	mgm.	*mgm.*
1. Kaolin	1.0	47.9
2. Kaolin + 0.27 per cent α-$Al_2O_3 \cdot 3H_2O$	2.2	61.9
3. Kaolin + 0.67 per cent α-$Al_2O_3 \cdot 3H_2O$	1.43	57.2
4. Kaolin + 7.58 per cent α-$Al_2O_3 \cdot 3H_2O$	11.8	77.1
5. Kaolin + 0.33 per cent α-$Al_2O_3 \cdot 3H_2O$ + 0.63 per cent α-Fe_2O_3	2.49	69.3
6. Kaolin + 0.5 per cent α-Fe_2O_3	1.83	52.5
7. Kaolin + 1.25 per cent α-Fe_2O_3	3.01	55.7
8. Kaolin + 10.74 per cent α-Fe_2O_3	13.6	65.5
9. Kaolin + 21.5 per cent α-Fe_2O_3	29.05	75.7

a confused flocculation of clay particles occurs and no evidence of the presence of a structure possessing vectorial properties is observed.

On the other hand, the elimination of iron and aluminum oxides from the surface of clay particles increases the ability of these particles to aggregate. A suspension of Na-clay (clay "Toida") was treated with Tamm's reagent (18) in order to eliminate iron oxides. The clay precipitate was washed with a 2 per cent NaOH solution and then with pure water, and, finally, it was purified by dialysis. Microscopic examination of this precipitate showed the beginning of structure formation, as evidenced by rotational movement. This was the so-called "rodlike" ["bâtonnet" of Friedel (5)] structure, modified here and there to a cylindric shape with rounded ends. The "rods" disappear between the Nicol prisms along the longitudinal axis (pl. 4, fig. 3) when they form in a liquid so viscous that they cannot move and unite with one another. The rods are optically homogeneous and show positive double refraction.

The structure of the Na-clay before treatment with Tamm's reagent is shown in plate 4, figure 4. The distinctive features of this structure, which characterize the alterations occurring in clay under the influence of the admixture of iron oxides, are negative double refraction, indicating a reconstruction of the micella, and the beginning of a structure formation bearing a close resemblance to the intermediate type of "conic" and "fanlike" structure of mesomorphous bodies (5).

Sufficiently thin envelopes of iron and aluminum oxides on clay particles possess cementing properties, and their action resembles that of intercrystalline layers between the grains of pure metals. In the absence of these interlayers, nothing would hinder the formation of one crystal from the individual particles. According to the general law, increase of the thickness of this interlayer leads to a decrease of cohesion. The accumulation of oxides at the surfaces of the adjoining particles exceeds the optimal dimension of the film, weakens the ability of the particles to aggregate, and gradually leads to their disaggregation.

SUMMARY

The nature of mixed clay-sand and clay-humus formations is explained, and structures are described which show that clay is the structure-forming component of soil.

Admixtures of iron and aluminum oxides to clay hinder the aggregation of clay particles. The presence of oxides in large amounts destroys the orienting properties of clay in respect to humus. In this case, mere coagulation occurs with a confused distribution of particles.

The elimination of iron and aluminum oxides from the surface of clay particles increases the ability of these particles to aggregate. A particular "rod" structure arises, the "rods" being optically homogeneous and possessing positive double refraction.

REFERENCES

(1) BERNIKOV, V. V. 1930 Influence of cations adsorbed by soil on certain mechanical and ultra-mechanical fractions obtained by elutriation. *Trans. Siberian Inst. Agr. Forestry Omsk* 13: 21–59 [Russian].

(2) DUMONT, I. 1909 Les enduits de revêtement des particules terreuses. *Compt. Rend. Acad. Sci.* [*Paris*] 140: 1067–1089.

(3) FERSMAN, A. E. Compounds of a changing composition in the crust of the earth. Collection of papers in honor of the twenty-fifth anniversary of the scientific activities of V. I. Vernadsky [Russian]. Leningrad.

(4) FRICKE, R., AND MEYRING, K. 1933 Zur Alterung junger Aluminiumhydroxydgele. *Ztschr. Anorgan. u. Allg. Chem.* 214: 269–274.

(5) FRIEDEL, G. 1922 Les états mésomorphes de la matière. *Ann. Phys.* [Paris] 18: 273–474.

(6) HALL, A. D. 1912 The Soil. Dutton, New York.

(7) HARDY, F. 1928 Studies in tropical soils. *Jour. Agr. Sci.* 24: 59.

(8) HELTZER, F. J. 1937 The rôle of organic substance in the formation of soil structure. *Chemization Socialist Agr.* 8: 53–63 [Russian].

(9) MATTSON, S. 1937 The electrochemistry of soil formation. *Ann. Agr. Col. Sweden* 4: 1–54.

(10) MEYERS, H. E. 1937 Physicochemical reactions between organic and inorganic soil colloids as related to aggregate formation. *Soil Sci.* 44: 331–358.

(11) MOGEIKO, A. M. 1930 Solonetzic chestnut soils of Ukraine and their chemical melioration. *Irrigation Com. Acad. Sci. U. S. S. R. Bul.* 6: 175–225 [Russian].

(12) NABOKIKH, A. I. 1916 On the Technique of Field and Laboratory Investigation of Soil Aggregates [Russian]. Odessa.

(13) SCHLOESING, TH. 1874 Études sur la terre végétale. *Ann. Chim. et Phys.* 15 (ser. 2): 514–546.

(14) SHOREY, E. C. 1929 Report on the determination of organic matter from the laboratories of soil fertility investigations, Bureau of Chemistry and Soils, U. S. Department of Agriculture. *Trans. Second Comn. and Alkali-Subcomn. Internatl. Soc. Soil Sci.* 5 (B): 87–92.

(15) SIDERI, D. I. 1936 On the formation of structure in soil: II. Synthesis of aggregates. On the bonds uniting clay with sand and clay with humus. *Soil Sci.* 42: 461–480.

(16) SIDERI, D. I. 1938 On the analysis of soil structure by the use of the colloid-chemical method of separation [Russian]. In print.

(17) SOKOLOVSKY, A. N. 1921 Phenomena of the colloid fraction of the soil. *Rept. Petrovsk. Agr. Acad.* 1–4: 85–225 [Russian].

(18) TAMM, O. 1922 Eine Methode zur Bestimmung der anorganischen Komponente des Gelkomplexes im Boden. *Meddel. Statens Skogsförsöksanst.* [Sweden] 19: 385–404.

(19) TYULIN, A. TH. 1937 The composition and structure of soil organo-mineral gels and soil fertility. *Soil Sci.* 45: 343–357.

(20) TYULIN, A. TH., AND MALOMAKHOVA, T. A. 1935 Separation of soil colloids by the method of fractional peptization. *Works All-Union Fert. and Agro-Tech. Res. Inst.* 2: 3–33 [Russian].

(21) TIURIN, I. V. 1926 The organic substance of soil and its rôle in soil-formation and fertility. Works of the May Session of the Academy of Science of U. S. S. R. *Soil Sci. and Agrochem.*, p. 104–124 [Russian].

(22) VILENSKI, D. G., AND GERMANOVA, V. N. 1934 Experimental study of the problems of structure formation. *Pedology* 29: 1–59 [Russian].

(23) WEISER, H. B., AND MILLIGAN, W. O. 1935 The constitution of hydrous oxide sols from x-ray diffraction studies. *Jour. Phys. Chem.* 40: 1–7.

(24) WEISER, H. B., AND MILLIGAN, W. O. 1935 X-ray studies on the hydrous oxides: V. *Jour. Amer. Chem. Soc.* 57: 238–241.

(25) WILLIAMS, W. R. 1920 Obshchee Zemledelie [General Agriculture: I. Theory of Soil Tillage]. Moscow.

PLATE 4

THE STRUCTURE OF CLAY AND OF CLAY-SAND AND CLAY-HUMUS MIXTURES

FIG. 1. Clay-sand mixture. Polarized light. Magnification × 40.

FIG. 2. Clay-humus mixture. Polarized light. Magnification × 53.

FIG. 3. Clay "Toida" after treatment with Tamm's reagent. Rodlike structure. Polarized light. Magnification × 40.

FIG. 4. Clay "Toida" before treatment with Tamm's reagent. Polarized light. Magnification × 40.

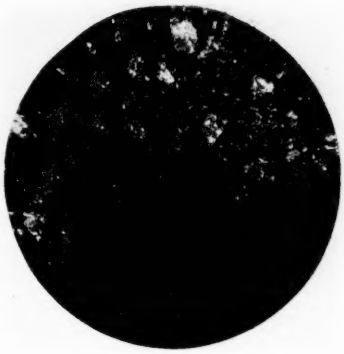

FIG. 1

FIG. 2

FIG. 3

FIG. 4

MICROBIAL ACTIVITIES IN SOIL: V. MICROBIAL ACTIVITY AND ORGANIC MATTER TRANSFORMATION IN PALOUSE AND HELMER SOILS[1]

S. C. VANDECAVEYE AND H. KATZNELSON[2]

Washington Agricultural Experiment Station

Received for publication December 27, 1937

The marked difference in type of microflora in the Palouse and Helmer soils discussed in the preceding paper in this series (23) suggested further studies of the microbial activity in these soils. The particular activity of the microflora and the nature of organic matter transformation resulting from additions of the surface organic residue of one soil to the other, as well as to its homologous soil, and the possible influence these factors may have in differentiating inherent properties of soils developed from the same parent material under similar climatic conditions form the principal objects of the work presented in the present paper.

EXPERIMENTAL PROCEDURE

Following the removal of the undecomposed organic residues from the surface, a suitable quantity of soil taken to a depth of 10 inches from each of the virgin areas of the Helmer and Palouse soils located near Troy, Idaho, and used for the previous experiment was brought to the laboratory. Duff covering the Helmer soil and litter covering the Palouse soil were also collected. The Helmer soil duff layer, varying from 0.5 to 1.5 inches in thickness, consisted chiefly of twigs and coniferous tree needles in various stages of decomposition. The Palouse soil litter, consisting of a very thin irregularly distributed layer of organic residue, was composed largely of grass vegetation in various stages of decomposition. These residues were air dried and finely ground. The soils were air dried and were then sifted through a 16-mesh sieve to effect thorough mixing and also removal of the coarse organic particles, and determinations were made of the hygroscopic moisture and normal field moisture capacities. The hygroscopic moisture for the Helmer and the Palouse soils was 2.11 and 2.12 per cent respectively, and the normal field moisture capacity was 26 and 25 per cent respectively.

Three 2.5-kgm. samples were taken from the bulk of each soil and placed in brown bottles covered with paper to exclude light and prevent excessive growth of algae and higher plants. Sufficient water was added to the bottles

[1] Published as Scientific Paper No. 374, College of Agriculture and Experiment Station, State College of Washington.

[2] Professor of soils and research assistant respectively.

to bring the soils to their normal field moisture capacity, which is virtually a static moisture condition with respect to capillary and gravitational movements and is also optimum for plant growth. The bottles were allowed to stand for 4 days to insure uniform distribution of the moisture and to give the microflora a chance to resume normal functioning. The normal field moisture capacity of the soils was maintained within narrow limits throughout the experiment by the addition of water when necessary.

On the fourth day each soil was passed through a 16-mesh sieve several times to insure homogeneity and was treated as follows:

SOIL NUMBER	SOIL TYPE	TREATMENT	
			*gm.**
1	Helmer silt loam	None	
2	Helmer silt loam	Helmer soil duff (0.578 per cent N)	20.000
		NH_4NO_3 (34.9 per cent N)	1.387
3	Helmer silt loam	Palouse soil litter (0.703 per cent N)	20.000
		NH_4NO_3 (34.9 per cent N)	1.316
4	Palouse silt loam	None	
5	Palouse silt loam	Palouse soil litter (0.703 per cent N)	20.000
		NH_4NO_3 (34.9 per cent N)	1.316
6	Palouse silt loam	Helmer soil duff (0.578 per cent N)	20.000
		NH_4NO_3 (34.9 per cent N)	1.387

* Per kilogram of soil.

The finely ground residues reinforced with sufficient ammonium nitrate to make the total nitrogen content equivalent to 3 per cent, thus insuring an ample supply of available nitrogen for maximum microbial activity during the process of organic matter transformation, were mixed thoroughly with the soil at the rate of 2 per cent on the dry soil basis. The mixing was accomplished first by hand and finally by passing several times through a 16-mesh sieve. Samples of soil were then removed for analysis, and the remaining portions, equivalent to 2 kgm. of oven-dried soil, were returned to the bottles, packed by gently tapping the bottles on the table, and connected with an absorption train for CO_2 determination.

The experiment was carried on at room temperatures fluctuating between 18 and 25°C. The numbers of bacteria, actinomyces, fungi, aerobic cellulose-decomposing bacteria, *Azotobacter*, and anaerobic nitrogen-fixing bacteria; CO_2 evolution; oxidation-reduction potentials; and pH values were determined at the beginning and at intervals of 2 or 3 days until maximum microbial counts were obtained. The intervals were then gradually increased to 5, 7, 14, and 30 days.

Chemical analyses were made at intervals for total, nitrate, and ammonia nitrogen as well as for total, hot-water-soluble, sulfuric-acid-soluble, and sulfuric-acid-insoluble carbon and nitrogen. These substances were determined:

A, at the beginning of the experiment; B, 40 days later, when maximum microbial numbers had been obtained; C, at 104 days; and D, at 235 days, when the experiment was terminated. At each sampling time, amounts equivalent to 250 gm. of oven-dried soil were removed, air dried, and stored for subsequent consecutive analysis.

Both the microbial and the chemical analysis were carried out in order to ascertain the relationship between specific groups of microbes and the activity of these groups in influencing the disappearance or accumulation of various chemical components of the soil and, conversely, the effect of these substances in stimulating or inhibiting the development of individual groups of soil microbes. The determination of pH values and of oxidation-reduction potentials was intended as an aid in the interpretation of the results of the microbial activity in the mineralization of organic matter.

At each sampling period the soil from each bottle was passed twice through a 6-mesh sieve to clean paper before the required amount of soil was removed. This treatment was intended to insure thoroughly mixed representative samples and also to prevent the development of anaerobic conditions in the bottles during the course of the experiment. The samples removed for analysis were spread very thinly on clean paper and thus were air dried quickly. The remainder of the soil was returned to the bottles and packed by gentle tapping of the bottles on the table. Water was added when necessary to maintain the moisture content at normal field moisture capacity. The bottles were then reconnected to the CO_2 absorption train.

Immediately after the samples were air dry, 1-gm. portions of soil were used for suitable dilutions of water suspensions for triplicate platings on agar prepared with the proper selective nutrient media for the determination of numbers of bacteria, actinomyces, and fungi. Other suitable portions were spread on triplicate silica gel plates impregnated with the proper nutrient solutions for the determination of numbers of *Azotobacter*, aerobic cellulose-decomposing bacteria, and anaerobic nitrogen-fixing bacteria. The remaining portions of the air-dried samples were used for determinations of pH values and oxidation-reduction potentials. The details of procedure in these methods and in the method for CO_2 determinations are described in a preceding paper in this series (22).

The analyses for total and nitrate nitrogen, and for total and various fractions of organic carbon of the soil samples taken at the A, B, C, and D periods were made also according to the methods described in a preceding paper (23). The ammonia nitrogen was determined by Nesslerization of a 0.01 N H_2SO_4 extract, the acid solution being used to replace any ammonia in the base-exchange complex of the soils.

The method of Waksman and Stevens (29) with the following modifications was used for the fractionation of the organic materials of the soils under investigation. Waksman (25) and others found that fats, resins, and waxes are very resistant to decomposition; hence these fractions were not deter-

mined. Only two extractions—the hot water, and the 72 per cent sulfuric acid—were made. They include the most readily attacked and therefore most important compounds influencing microbial activity.

Inasmuch as the interest in the organic matter transformations in this investigation was focused chiefly on the changes in the organic carbon as affected by microbial activity in the soil, another modification was adopted. The total organic carbon content, instead of reducing sugars, was determined in the extracts as well as in the extracted soil residues and in the unextracted soil. When it is found, for example, that the hot-water-soluble carbon and the sulfuric-acid-soluble carbon in the soil decrease with time, the decreases are explainable only by the fact that a part of the constituents represented by these fractions was destroyed or utilized by the soil microflora. These decreases can be expressed in terms of carbon instead of in terms of sugars, hemicelluloses, or celluloses, as the case may be. It may be objected that the total carbon determinations of hot water or sulfuric acid extracts include carbon from materials other than carbohydrates. Even with these components included, it appears that this method is more suitable for the purpose intended here than is a determination of the reducing sugars in these extracts, for the latter method does not account for certain water-soluble compounds, including starches and dextrines, which are not completely hydrolyzed to reducing sugars, and certain organic acids and other organic compounds which are certainly present in the acid if not in the water extracts. A total carbon determination accounts for all these constituents in terms of carbon and obviates the necessity of using factors in calculating the organic matter content of the soil, factors which, incidently, may vary considerably, according to Waksman and Hutchings (27).

EXPERIMENTAL RESULTS

Carbon dioxide evolution

The data on CO_2 production by each soil during the course of the experiment are presented in figures 1 and 2, which indicate a profuse evolution of CO_2, particularly from the soils treated with 2 per cent organic residue. The maximum daily CO_2 production occurred the first day of the experiment, and secondary peaks appeared 10 to 12 days later, suggesting a possible rhythmic variation in the activity of the microflora. Secondary peaks in CO_2 production have been noted by other investigators. Melin (10) observed them in the decomposition of certain organic residues, but they occurred about 30 days after the initial maximum evolution, which took place during the first two or three days. He explains the first peak on the basis of rapid decomposition of the readily available water-soluble constituents and the second by assuming a more active decomposition of the less decomposable constituents such as celluloses and hemicelluloses. Johannson (8), who obtained similar results, attributes the fluctuations in CO_2 production to rhythmic variations in microbial activity, on the assumption that periodic fluctuations occur in

the rate of metabolism and the growth velocity of soil microbes. Smith et al. (16) noted that after the initial maximum production of CO_2 had taken place in soils kept in the laboratory at optimum moisture and temperature conditions, a rather definite rhythmic periodicity in evolution of CO_2 occurred, but they did not correlate this periodicity with microbial activity as determined by numbers of organisms. Although they concede the possibility

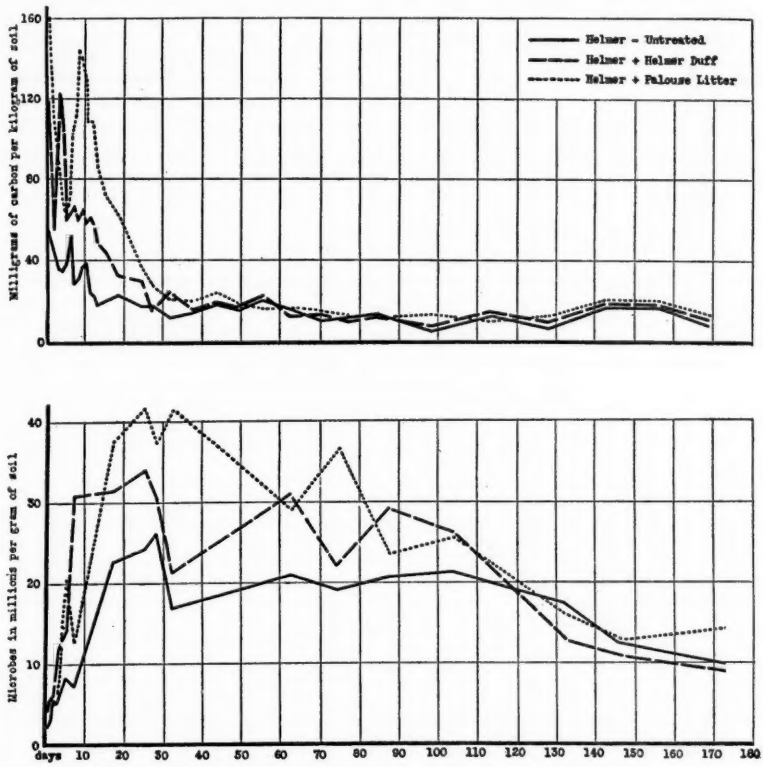
Helmer - Untreated
Helmer + Helmer Duff
Helmer + Palouse Litter
Milligrams of carbon per kilogram of soil
Microbes in millions per gram of soil
days

FIG. 1. CARBON DIOXIDE PRODUCTION AND NUMBER OF MICROBES IN VARIOUSLY TREATED HELMER SILT LOAM

of periodic variations in the rate of respiration between the logarithmic growth and logarithmic death phases of microbes, they consider it difficult to conceive that the generation time and the metabolic processes of a mixed culture of microbes which constitutes the soil microflora are sufficiently similar to produce regular periodic fluctuations in the rate of CO_2 production.

No correlaton was evident between the irregular fluctuations in CO_2 evolution from the variously treated Helmer and Palouse soils and the microbial

activity as indicated by the numbers of organisms present at the time when these fluctuations were most apparent. Furthermore, a comparison of the data in figures 1 and 2, which present graphically both the amounts of CO_2 produced and the numbers of microbes present in these soils at various periods of sampling, discloses that the maximum numbers of organisms did not appear until some time after a sharp decline in CO_2 evolution had taken place. A

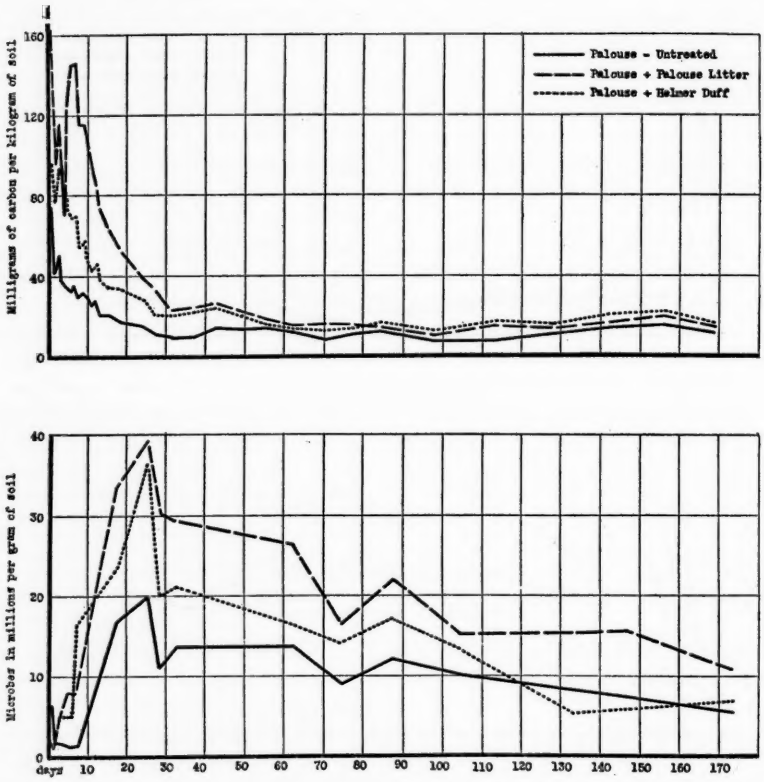

FIG. 2. CARBON DIOXIDE PRODUCTION AND NUMBER OF MICROBES IN VARIOUSLY TREATED PALOUSE SILT LOAM

sharp reduction in CO_2 production generally occurred at or before the tenth day of the experiment, and this was followed by a more gradual decline, until after 30 days a low but fairly uniform production resulted. The maximum numbers of microbes did not appear until 25 to 30 days had passed. That there is a definite lag between maximum CO_2 production and maximum numbers of microbes during the early stages of decomposition of readily decom-

posable organic residues in the soil, cannot be doubted. The data in figures 1 and 2 indicating this lag are amply supported in two previous publications (21, 22) and also by the work of Jensen (6), Romell (15), and others. Although different soils do not respond alike to various organic residues, the lapse of time between maximum CO_2 evolution and maximum microbial development is too great to warrant dependence on the rate of CO_2 production as an accurate measure of microbial numbers determined by plate counts. The available data and the explanations of other investigators referred to in a previous paper (22) are inadequate to account fully for the cause and significance of this protracted lag period.

The peaks in the CO_2 curves in figures 1 and 2 show that during the first 10 days of the experiment the Palouse soils were more active than the similarly treated Helmer soils. The total CO_2 production in comparable samples was

TABLE 1

Total CO_2 production and carbon-nitrogen relationships in the various soils and organic residues, based on dry weight

NUMBER	1	2	3	4	5	6	7	8
Substance	Helmer untreated	Helmer + Helmer duff	Helmer + Palouse litter	Palouse untreated	Palouse + Palouse litter	Palouse + Helmer duff	Helmer duff	Palouse litter
CO_2 in mgm. of C per kgm. of soil	783.07	1,344.51	1,908.72	788.46	1,953.39	1,332.13	.....	.....
Total C, *per cent*	2.317	3.345	3.319	3.460	4.304	4.177	36.69	32.64
Total N, *per cent*	0.100	0.161	0.170	0.209	0.277	0.271	0.578	0.703
C:N ratio	23.17	20.78	19.53	16.54	15.53	15.41	63.45	46.39
Water-soluble C, *per cent*	0.074	0.144	0.156	0.117	0.198	0.156	2.542	1.765
H_2SO_4-soluble C, *per cent*	0.613	0.840	0.900	0.969	1.287	1.257	9.919	16.886
H_2SO_4-insoluble C, *per cent*	1.619	2.168	2.181	2.264	2.517	2.627	22.779	12.262
H_2SO_4-insoluble N, *per cent*	0.057	0.057	0.060	0.092	0.101	0.100	0.304	0.269
Protein N,* *per cent*	0.105	0.135	0.139	0.210	0.237	0.236	0.569	0.605

*Sum of H_2SO_4-soluble and H_2SO_4-insoluble nitrogen.

approximately the same, however, as is indicated in table 1, in which data are presented on total CO_2 production and on the carbon-nitrogen relationships and carbon fractions of the various soils and organic residues. The greater quantities of water-soluble and sulfuric-acid-soluble carbon in the Palouse soil and Palouse litter may explain these higher peaks, since it is well recognized that these fractions of the organic material in the soil are attacked first. The effect of Palouse litter on CO_2 evolution in soil 3 as compared with that of Helmer duff in soil 6 is clearly evident.

Microbial analysis

The periodical counts of bacteria, actinomyces, fungi, and aerobic cellulose-decomposing bacteria are illustrated graphically in figures 3, 4, 5, and 6.

A consideration of the bacterial counts recorded in figure 3 and of the total

numbers of microbes illustrated in figures 1 and 2 indicates that, in general, both were considerably lower in the Palouse than in the Helmer soils. In regard to the untreated samples this is contrary to the results reported in the preceding paper (23), which shows that under field conditions both the total microbial population and the population of bacteria were greater in the Palouse soil than in the Helmer soil at the three depths sampled at different times of the year. The effect of the constant optimum moisture and temperature conditions obtaining in the laboratory as compared with the fluctuating temperatures and moisture contents of the soils under their natural

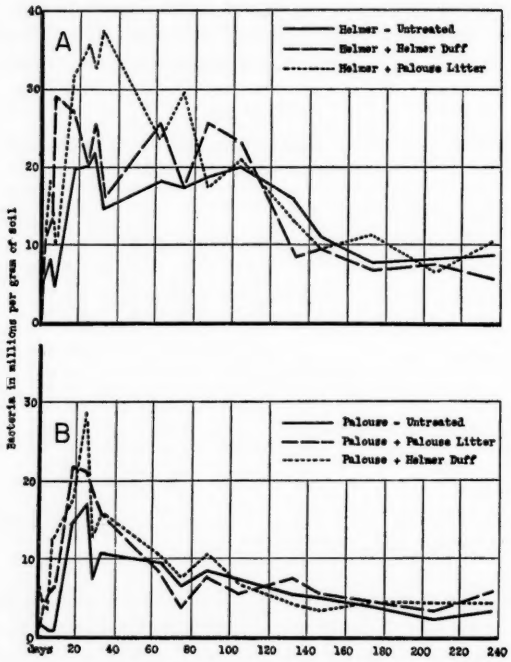

FIG. 3. BACTERIA IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

environment offers a plausible explanation for the observed differences in bacterial behavior. The general rise in bacterial numbers in the untreated samples between the fifth and the twenty-fifth day in the laboratory strengthens this assumption, although a part of this increased activity was due to the decomposition of root material which constitutes a part of the living vegetation under field conditions.

The addition of Helmer duff or Palouse litter to the soils greatly stimulated the development of bacteria during the early stages of organic matter trans-

formation. This effect diminished sharply after the first 15 to 30 days, particularly in the Palouse soils. Some minor peaks in bacterial numbers occurred later in the Helmer soils in which the greater initial stimulating effect of the organic residues was manifested. The Palouse litter in the Helmer soil was considerably more effective in stimulating bacterial growth than was the Helmer duff, but this was not true in the Palouse soil. There the effect of the two residues tended to be in the reverse order, but the difference is small if it is considered that the one exceptionally high count occurring on the twenty-fifth day in soil 6 (Palouse soil treated with Helmer duff) may have

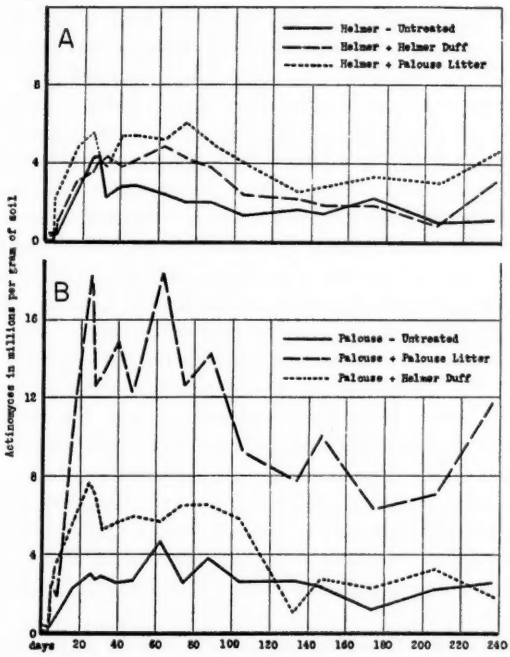

FIG. 4. ACTINOMYCES IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

been partly the result of experimental error. The difference in bacterial activity appeared to be principally the result of differences in the nature of the humus and organic residues in the two soils. The composition of these substances varied considerably, as may be noted from the data in table 1.

The activity of actinomyces, which is portrayed in figure 4, is interesting. Their growth, like that of the bacteria, was markedly stimulated by the addition of either organic residue to the soil, but the effect of these materials persisted for a longer time. The numbers of actinomyces were smaller in the untreated Helmer soil than in the untreated Palouse soil, the difference

being in accordance with that observed under field conditions, as reported in the preceding paper (23). Both the inherent character of the soil other than reaction and the nature of the organic residues added were strikingly reflected in their effect on the activity of these organisms. Not only were their numbers much smaller in the Helmer than in the Palouse soil irrespective of treatment, but the difference in effect of the two residues was also very pronounced. The addition of Palouse litter to Palouse soil was exceedingly stimulating, as it caused about a fourfold increase in numbers at the peak of its influence as compared with not much more than a twofold increase resulting from the Helmer duff. The difference was not so marked in the Helmer soil. There the addition of Palouse litter resulted in about a twofold increase in numbers of actinomyces during the period when its influence was most pronounced, and the effect of Helmer duff in this respect was somewhat less.

The actinomyces as a group are recognized as being capable of utilizing a wide variety of carbon compounds and protein substances as sources of carbon and energy. It may be noted from the data in table 1 that the sum of the water-soluble and sulfuric-acid-soluble carbon as well as the amount of protein nitrogen is greater for soil 4, the Palouse soil, than for soil 1, the Helmer soil. The larger quantity of these carbon and nitrogen substances may explain the larger numbers of actinomyces in the Palouse soil. A more careful analysis of the data in table 1 strengthens this point. Both the sum of the water-soluble and the sulfuric-acid-soluble carbon and the amount of protein nitrogen are shown to be greater for the Palouse litter than for the Helmer duff. The Palouse litter proved to be the more effective of the two residues in stimulating actinomycete growth. Soil 5, the Palouse soil with Palouse litter added, had the largest amounts of water-soluble and sulfuric-acid-soluble carbon and protein nitrogen; it also had the greatest actinomycete counts. The same correlation holds for the other treatments, showing the definite influence of the nature of the soil humus and the organic residues added to the soils on the activity of these organisms. The relatively small differences in reaction of the soils which are indicated in figure 9 are unimportant in this respect.

Large numbers of actinomyces are present in both soils. Their activity, therefore, should play an important part in organic matter transformation, at least in certain cases as will be shown later, although some investigators ignore their presence in the soil and their rôle in decomposition processes. The more recent work of Itano and Arakawa (9), however, emphasizes their importance in biological processes in the soil.

The fungus population, as may be noted from figure 5, was not nearly so large in any of the soils as were the bacterial and actinomycete populations, but it is evident that the Helmer soil is a much better medium for fungus growth than is the Palouse soil. This is shown by the graphs for the untreated soils as well as those for the treated soils and is in agreement with the observations reported previously (23). Both the Palouse litter and the Helmer duff

stimulated markedly the growth of fungi for about the same length of time as they stimulated the growth of actinomyces. These materials exerted a much more pronounced effect in the Helmer than in the Palouse soil, as during the period of maximum influence they resulted in approximately a threefold increase in numbers of fungi in the Helmer soil and roughly a twofold increase in numbers in the Palouse soil. The stimulating effect of the Helmer duff was greater in both soils than was that of the Palouse litter, indicating that the former is a better food for fungi. Evidently, the nature of the residue on

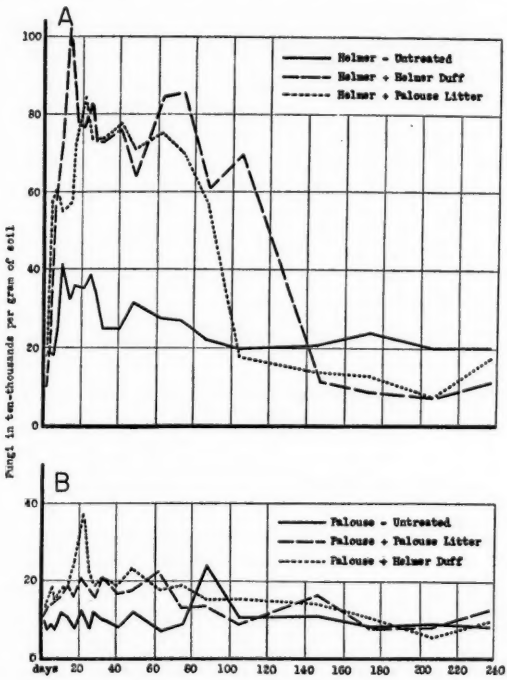

FIG. 5. FUNGI IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

the floors of coniferous forests and the nature of the humus formed from this residue are such as to stimulate fungus growth. Many investigators, including Waksman, et al. (31), Cobb (2), and Powers and Bollen (14), have found that the coniferous floor has large numbers of fungi and that in many cases these forms are the predominating ones in the surface layers.

The cellulose-decomposing bacteria, which were not numerous and which never attained significant numbers in the untreated soils, began to multiply in the treated soils after the maximum peaks had been reached by the other groups of microbes. The data, presented in figure 6, show that the Palouse

soils had the higher numbers and that the variations in effect caused by the two organic residues added to the different soils were not particularly significant. The increases in numbers of cellulose-decomposing bacteria will be discussed later.

The anaerobic nitrogen-fixing bacteria, although present in both soils, never attained large numbers. The importance of their activity here is, therefore, doubtful. On the whole, their development was not stimulated to any sig-

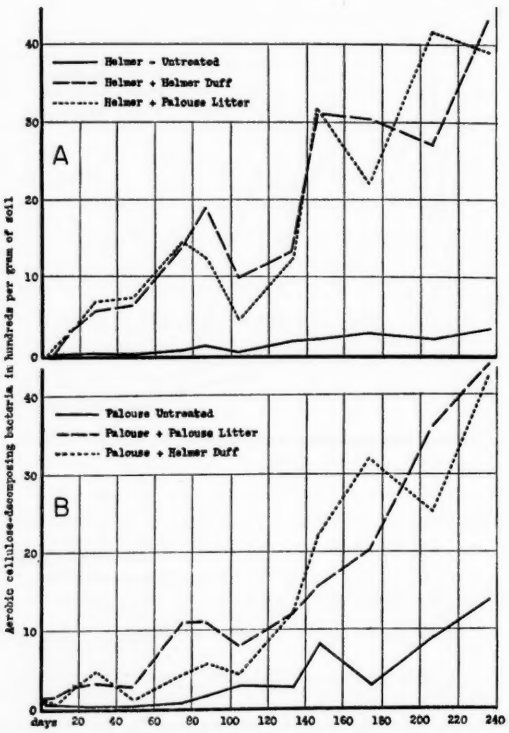

FIG. 6. AEROBIC CELLULOSE-DECOMPOSING BACTERIA IN (A) HELMER SILT LOAM AND IN (B) PALOUSE SILT LOAM

nificant degree by the addition of the two organic residues to the soils. Since their numbers, which fluctuated from a few to 200 per gram of dry soil, were about the same as those reported for the same soils in the previous paper (23), they have been omitted here. As stated also in the previous paper, the *Azotobacter* species was not found in these soils.

An examination of figures 3 to 6 discloses not only the influence of the organic food supply and of the soil properties on the type of soil microflora and on the

activity of specific groups of organisms, but also a certain sequence in the activity of the various specific groups of soil microbes. The fungi, except where the numbers were small, attained their peaks in 10 to 15 days. The bacteria reached maximum numbers in 15 to 30 days, depending on the soil. The actinomyces began to reach highest counts only after 25 or more days. The cellulose-decomposing organisms did not greatly increase in numbers until the activity of the other three groups had subsided. It seems evident that both the fungi and the bacteria, particularly the former, were able to compete successfully with the actinomyces for the readily available (probably water-soluble) food supply. The actinomyces, probably suppressed for a short time when readily available food was plentiful, began to rise in numbers when the fungus population and in some cases the bacterial population began to decline. In about 40 days when, as shown in tables 2 and 3, the supply of water-soluble carbon was reduced considerably and the sulfuric-acid-soluble carbon, as well as the water- and acid-soluble nitrogen, was still not materially affected, the aerobic cellulose-decomposing bacteria began to multiply rapidly. The food supply evidently was ample and its nature suitable for their continually increasing multiplication until the termination of the experiment.

Sequential activity of specific groups of microbes in the soil was noted in previous work (21) and has been reported also by Norman (11), Waksman and Starkey (28, pp. 75–101, 244–245), and others. The sequence in activity, the effect of certain groups of organisms on others, and the influence of the nature of the food supply on various specific groups of organisms which were evident in this work are in general agreement with the observations of these investigators.

Organic matter fractionations, pH values, and oxidation-reduction potentials

The results of the carbon and nitrogen analyses of the various soil extracts intended for fractionation of the organic matter in the six soils at the A, B, C, and D periods mentioned in the experimental procedure are summarized in tables 2 and 3. The relative changes affecting the carbon and nitrogen in the various soil extracts during the course of the experiment are illustrated in figures 7 and 8, in which the amounts of carbon and nitrogen present in the various organic matter fractions at successive time intervals are presented in percentages of the amounts present at the beginning of the experiment.

It is noted in table 2 that in certain soil samples the sum of the percentages of carbon in the various fractions accounts for more than the total, indicating some limitations of the analytical methods used. In most samples, however, the sum of the percentages of carbon in the various fractions ranges between 95 and 99 per cent of the total, showing that the results obtained by the use of the analytical methods as described in the experimental procedure are at least as reliable as those indicated by the available data on sugar determinations in the water- and acid-soluble fractions. The sum of the percentages of nitrogen in the various extracts listed in table 3 also exceeds the total amount

of nitrogen in the soil in some cases, but, on the whole, the results show a satisfactory recovery of nitrogen by this method of fractionation.

Various investigators including Starkey (17), Waksman and Tenney (30), Tenney and Waksman (20), and Hutchings and Martin (5) hold that the rate of decomposition of organic residues depends upon their chemical composition. For example, residues rich in nitrogen and relatively poor in cellulose,

TABLE 2

Organic carbon fractions, in per cent of oven-dried soil

SOIL NUMBER*	TOTAL C	WATER-SOLUBLE C	H_2SO_4-SOLUBLE C	H_2SO_4-INSOLUBLE C	SUM OF C FRACTIONS	PER CENT OF TOTAL C ACCOUNTED FOR
A 1	2.317	0.074	0.613	1.619	2.306	99.52
2	3.345	0.144	0.840	2.168	3.152	94.24
3	3.319	0.156	0.900	2.181	3.237	97.53
4	3.460	0.117	0.969	2.264	3.350	96.83
5	4.304	0.198	1.287	2.517	4.002	92.69
6	4.177	0.156	1.257	2.627	4.040	96.71
B 1	2.145	0.080	0.645	1.582	2.307	107.58
2	3.253	0.111	0.796	2.331	3.238	99.48
3	3.204	0.117	0.850	2.032	2.999	93.61
4	3.529	0.087	1.128	2.253	3.468	98.29
5	3.937	0.129	1.278	2.464	3.871	98.31
6	4.025	0.138	1.226	2.636	4.000	99.41
C 1	2.080	0.064	0.559	1.479	2.102	101.08
2	3.225	0.083	0.862	2.092	3.037	94.14
3	3.075	0.112	0.897	2.046	3.054	99.36
4	3.478	0.089	1.047	2.248	3.383	97.30
5	3.844	0.108	1.217	2.460	3.785	98.47
6	4.027	0.129	1.268	2.538	3.935	97.69
D 1	2.204	0.054	0.462	1.481	1.997	90.65
2	2.992	0.076	0.756	2.151	2.983	99.69
3	2.847	0.086	0.799	2.117	3.002	105.42
4	3.300	0.095	0.956	2.190	3.241	98.23
5	3.838	0.109	1.061	2.419	3.589	93.35
6	3.906	0.108	1.085	2.480	3.673	94.01

* Letters A to D indicate progressive periods of sampling: A, beginning; B, 40 days; C, 104 days; D, 236 days.

such as legume hays, decompose faster than materials relatively poor in nitrogen and rich in cellulose. Waksman and Starkey (28, pp. 75–101, 244–245) and Watson (32), among others, give evidence of the well-recognized fact that in the process of decomposition of organic materials the water-soluble fraction is attacked first, followed in order by the proteins, hemicelluloses, and celluloses. Decomposition then becomes less rapid, because of the relative increase

of the less easily decomposable substances, such as fats, waxes, resins, lignins, and synthesized microbial products which include some of these substances. The greater the amounts of the more readily available fractions in plant materials, as in young plants, for instance, the more rapid their decomposition should be. The composition and age of plant materials, however, are not the only factors influencing their decomposition. The types and numbers of

TABLE 3

Nitrogen fractions, in per cent of oven-dried soil

SOIL NUMBER*	TOTAL N	WATER-SOLUBLE† N	H_2SO_4-SOLUBLE N	H_2SO_4-INSOLUBLE N	NITRATE N	SUM OF N FRACTIONS	PER CENT OF TOTAL N ACCOUNTED FOR	PROTEIN‡ N
A 1	0.100	0.002	0.048	0.057	0.000	0.107	106.71	0.105
2	0.161	0.013	0.078	0.057	0.015	0.163	101.86	0.135
3	0.170	0.014	0.079	0.060	0.016	0.169	99.41	0.139
4	0.209	0.006	0.118	0.092	0.000	0.216	103.44	0.210
5	0.277	0.020	0.136	0.101	0.018	0.275	99.20	0.237
6	0.271	0.021	0.136	0.100	0.016	0.273	100.62	0.236
B 1	0.093	0.003	0.034	0.058	0.002	0.097	103.97	0.092
2	0.166	0.012	0.070	0.071	0.017	0.170	98.09	0.141
3	0.173	0.013	0.077	0.071	0.017	0.178	107.95	0.148
4	0.214	0.006	0.112	0.095	0.005	0.218	101.94	0.207
5	0.273	0.016	0.132	0.106	0.015	0.269	98.93	0.238
6	0.270	0.017	0.132	0.105	0.018	0.272	102.99	0.237
C 1	0.100	0.003	0.043	0.055	0.004	0.105	105.01	0.098
2	0.166	0.010	0.064	0.067	0.020	0.161	97.35	0.132
3	0.170	0.007	0.071	0.071	0.023	0.172	101.17	0.142
4	0.217	0.005	0.108	0.093	0.009	0.215	99.21	0.201
5	0.266	0.007	0.118	0.103	0.003	0.231	97.70	0.221
6	0.267	0.008	0.114	0.105	0.003	0.230	96.96	0.219
D 1	0.092	0.001	0.031	0.052	0.006	0.090	98.53	0.083
2	0.146	0.003	0.046	0.066	0.023	0.138	94.74	0.112
3	0.154	0.004	0.062	0.067	0.022	0.155	100.85	0.129
4	0.205	0.005	0.090	0.091	0.010	0.196	95.49	0.181
5	0.261	0.007	0.100	0.097	0.040	0.244	93.83	0.198
6	0.252	0.007	0.097	0.101	0.040	0.245	97.33	0.198

* Letters A to D indicate progressive periods of sampling: A, beginning; B, 40 days; C, 104 days; D, 236 days.

† Exclusive of nitrate nitrogen.

‡ Sum of the H_2SO_4-soluble and H_2SO_4-insoluble nitrogen.

microbes present also play a leading rôle in this process. It is generally accepted, for example, that fungi attack cellulose readily in the presence of available nitrogen, that bacteria decompose sugars readily even in the presence of small amounts of available nitrogen, and that actinomyces can utilize the

carbon of both carbonaceous and nitrogenous substances. Obviously, the mineralization of organic residues is a complex process depending on a variety

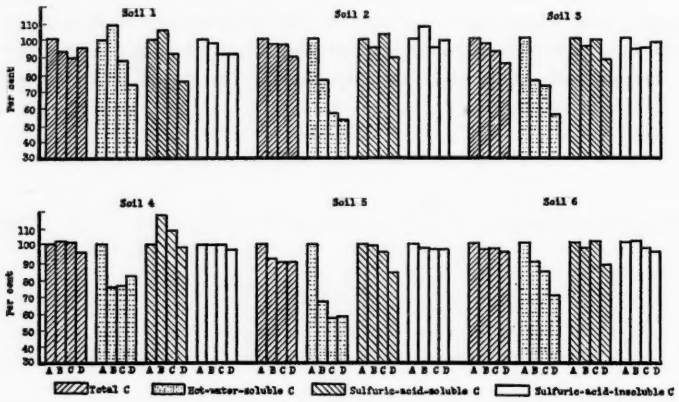

FIG. 7. ORGANIC CARBON FRACTIONS IN PERCENTAGES OF THE AMOUNTS PRESENT IN THE SOIL AT THE BEGINNING OF THE EXPERIMENT

A, at the beginning; B, at 40 days; C, at 104 days; and D, at 236 days

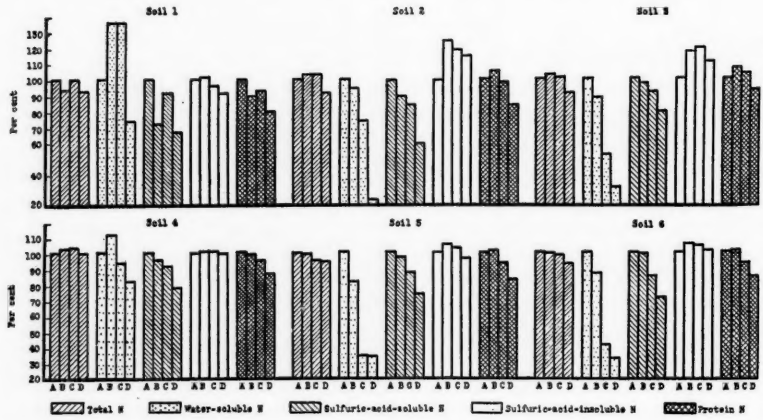

FIG. 8. NITROGEN FRACTIONS IN PERCENTAGES OF THE AMOUNTS PRESENT IN THE SOIL AT THE BEGINNING OF THE EXPERIMENT

A, at the beginning; B, at 40 days; C, at 104 days; and D, at 236 days

of closely related factors. Although most of the available evidence regarding the nature of organic matter decomposition is based on the results of experiments with small quantities of various organic residues, pure or heterogeneous,

used alone or mixed with sand, and inoculated with pure or mixed cultures of soil microbes, or soil suspensions, the soil serving merely as an inoculant and not as a medium for microbial activity, the results of this investigation, in which the soil was used as the medium for microbial activity, bear out at least some of the foregoing observations, as will be pointed out.

A comparison of the amounts of carbon and nitrogen in the untreated soils, soils 1 and 4, reveals that the Palouse soils contained more protein nitrogen, and more water-soluble and sulfuric-acid-soluble carbon and nitrogen than did the Helmer soils. The data in table 1 show that the Palouse litter also contained larger amounts of these carbon and nitrogen substances than did the Helmer duff, although probably a part of the readily available materials, such as water-soluble and possibly sulfuric-acid-soluble substances, had been decomposed already, since these residues were collected from the surface of the soils. The relationship of some of these compounds to the activity of the bacteria, fungi, and actinomyces in particular has already been pointed out.

The total carbon content as shown in table 2 and figure 7 decreased in all soils. This was to be expected, since CO_2, the most important measurable by-product in organic matter transformation in the soil, was liberated. An exact comparison of the loss of carbon with the amounts of CO_2 produced and the total numbers of microbes in the soil is not possible, because of the limitations of the analytical methods and also because different specific groups of microbes do not use equal quantities of the carbon liberated from the organic materials broken down by them. It is well known, for example, that the fungi as a group utilize liberated carbon more efficiently than do the bacteria as a group. Nevertheless, general relationships are evident. The soils which lost the largest amounts of carbon, as soils 2, 3, 5, and 6, also produced the largest total amounts of CO_2 and had the largest microbial populations, although as has been pointed out before, there was a considerable lag between maximum evolution of CO_2 and maximum numbers of organisms.

The data in table 2 and figure 7 also indicate that the water-soluble carbon in soils 2, 3, 5, and 6, which received the organic residues and contained the largest amounts of this carbon, decreased more rapidly and to a greater extent than did the other fractions. This is in accordance with the observations of the aforementioned investigators and of other workers in the field of organic matter transformation. The greatest loss of water-soluble carbon in all the soils, except soil 1, occurred in the earlier stages of decomposition during the A period when microbial activity, particularly that of the bacteria and fungi, was at a maximum. The discrepancy in soil 1 and, to a certain extent, that in soil 2 may be due to experimental error.

The sulfuric-acid-soluble carbon, which comprised 25 to 30 per cent of the total carbon, evidently was much more resistant to decomposition in the soil than was the water-soluble carbon. The sulfuric acid extract contains among other carbon compounds hemicellulose and cellulose. Since hemicelluloses are synthesized by soil microbes, it is likely that although the cellulose in

the sulfuric-acid-extracted fraction was decomposed rapidly, the newly synthesized hemicellulose accumulating as a by-product of microbial activity obscured the actual changes which took place in the carbon of this fraction. Although the percentage breakdown of carbon in this fraction was relatively small in comparison with that in the water-soluble fraction, the total amounts lost, as shown in table 2, are considerable, indicating that the sum total of the decomposing and synthesizing activities favored the former. Again the results obtained from soils 1 and 4 appear to be erratic, as they were with respect to the water-soluble carbon. If these discrepancies are disregarded, it is noted that the greatest loss occurred in soils 5 and 6 which, according to the data in figures 3 and 4, also had the largest numbers of actinomyces, as well as large numbers of bacteria. This suggests that the sulfuric-acid-soluble carbon fraction, which also contains considerable quantities of nitrogenous substances, as indicated in table 3, is, as has been pointed out, a more suitable food for actinomyces than for bacteria and fungi. The loss of sulfuric-acid-soluble carbon in these soils as well as in the other two receiving organic residues continued after 104 days, the C period. At that time the activity of the actinomyces declined rapidly and the numbers of aerobic cellulose-decomposing bacteria began to increase rapidly and continued their ascendency until the end of the experiment, evidently indicating that a plentiful supply of cellulose was still available at that time.

The sulfuric-acid-insoluble carbon fraction, which comprised from 63 to 74 per cent of the total carbon, contained some cellulose, lignins, and other difficultly decomposable compounds. The carbon in this fraction proved to be the most resistant to decomposition, a fact which is generally accepted. Although the percentage reduction of carbon in this fraction was small, regardless of treatment, and, therefore, was insignificant from this standpoint, the total amounts lost, as may be noted from the data in table 2, were as large as and in certain cases larger than those lost from the water-soluble fraction, indicating that some decomposition was taking place.

The data on the changes in nitrogen content of the various soil extracts obtained at the four successive sampling periods are presented in table 3 and figure 8. A small reduction in the supply of total nitrogen occurred during the course of the experiment. Since no *Azotobacter* and only a few anaerobic nitrogen-fixing bacteria were present in these soils, no increase in total soil nitrogen was expected. To be sure, the absolute accuracy of the Kjeldahl method may be questioned, but the observed loss of nitrogen, though small and difficult to account for, appeared to be too consistent to be accidental. Similar results obtained under similar conditions were reported in a previous publication (22) in which it was pointed out that the reduction in total nitrogen was not caused by the loss of ammonia, since no appreciable quantities of this substance were found to escape from the soil. The cause of the small loss of nitrogen observed in these experiments is still obscure.

The water-soluble nitrogen, as may be noted from figure 8, decreased rapidly

and to a marked extent in every soil, and particularly in the soils treated with organic residues. In some of the latter soils only a small percentage remained at the end of the experiment. The nitrogen in this fraction consisted of ammonia, amino acid, and water-soluble protein. It did not include nitrate nitrogen, as this was determined and accounted for separately. The ammonia nitrogen, although included in the water-soluble fraction, was also determined separately. The results of the determinations of both of these compounds are recorded in table 4.

The data in table 4 show that although the amounts of ammonia and nitrate nitrogen decreased rapidly during the early stages of decomposition of the organic residues in soils 2, 3, 5, and 6, an abundant supply was available at all times, even when microbial numbers were at a maximum. Moreover, it is evident that as the ammonia nitrogen decreased in quantity after the first 17 days the amounts of nitrate nitrogen increased rapidly, showing that nitrification in these soils was very active. Larger amounts of nitrate nitrogen

TABLE 4

Nitrate and ammonia nitrogen, in parts per million of oven-dried soil

DAYS	1		2		3		4		5		6	
	Helmer untreated		Helmer + Helmer duff		Helmer + Palouse litter		Palouse untreated		Palouse + Palouse litter		Palouse + Helmer duff	
	NO_3-N	NH_3-N	NO_3-N	NH_3-N	NO_3-N	NH_3-N	NO_3-N	NH_3-N	NO_3-N	NH_3-N	NO_3-N	NH_3-N
0	1.2	16.6	153.8	80.0	156.8	140.6	2.58	42.9	177.7	138.1	160.0	153.9
7	3.6	14.2	150.9	50.0	145.4	72.8	6.60	48.0	150.9	138.1	140.3	154.0
17	12.5	20.7	133.3	57.2	145.4	50.7	25.00	30.0	140.3	125.1	140.3	133.5
40	23.8	12.0	166.6	38.1	166.6	48.5	48.10	11.5	154.3	102.7	179.5	111.1
104	44.4	11.8	205.1	53.3	228.5	40.0	86.00	10.3	320.0	14.5	320.0	80.0
236	61.5	8.0	235.2	10.7	216.2	11.5	102.50	6.16	400.0	10.0	400.0	10.0

accumulated in the Palouse soils than in the comparable Helmer soils. This was to be expected, since in the former the C:N ratios were narrower, as indicated in table 1, and the amounts of water- and acid-soluble-nitrogen were larger than in the latter. It is noted also that during the first 40 days when the fungus population was largest, the ammonia in soils 2 and 3, the Helmer soils, disappeared more rapidly than in soils 5 and 6, the Palouse soils. Since the fungus population in the two Helmer soils was about three times as large as that in the two Palouse soils, it is likely that these organisms were responsible for the greater loss of ammonia from the Helmer soils. As indicated in figure 8, the nitrogen content of the sulfuric-acid-insoluble fraction in these two soils built up with time, whereas it did not change appreciably in the two Palouse soils. According to previous results (21) as well as to those of Waksman (24), Sturgis (19) and others, it appears that in the process of decomposition of organic residues in the soil the nitrogen content of the sulfuric-acid-insoluble fraction of the organic matter tends to increase as a result of

synthesis of microbial protoplasm. Both the Helmer and the Palouse soils supported a large bacterial flora, but apparently more microbial protoplasm was produced in the treated Helmer soils with their comparatively large fungus population and small numbers of actinomyces than in the similarly treated Palouse soils with their comparatively small fungus population and large numbers of actinomyces.

The sulfuric-acid-soluble nitrogen, as may be noted from the data in figure 8, decreased in about the same ratio in all the soils, indicating that the protein substances in this fraction of the organic matter in the various soils were

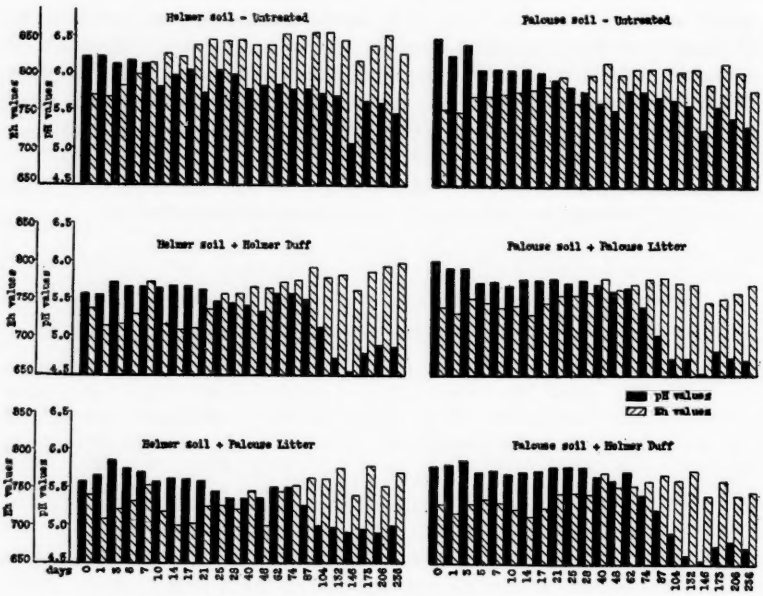

FIG. 9. Eh AND pH VALUES OF HELMER AND PALOUSE SILT LOAMS

The Eh values are the oxidation-reduction potentials calculated to a standard pH value of 2, using the correction factor of 80 millivolts per change of 1 pH unit [Peech and Batjer (12)]

attacked at approximately the same rate. The protein nitrogen, which comprises both the sulfuric-acid-soluble and -insoluble nitrogen decreased in about the same order as the sulfuric-acid-soluble nitrogen but to a smaller extent, as would be expected, since the sulfuric-acid-insoluble nitrogen did not decrease appreciably.

The pH values of the soils, determined at various sampling periods, are recorded in figure 9. The reaction of all the soils was on the acid side of neutrality, the treated soils being more acid than the untreated ones. The small differences in reaction, as such, did not appear to have any marked

influence in bringing about the observed differences in microbial activity. A consistent increase in acidity with time took place in all the soils. A similar increase in acidity noted in previous work (22) of a similar nature was attributed to the accumulation of nitrate nitrogen. Watson (32) also observed an increasing acidity of the soil as a result of organic matter decomposition processes. More recently Stephenson (18) found that changes in soil reaction under field conditions follow closely upon changes in nitrate nitrogen accumulation. The production of various organic acids in the process of organic matter decomposition is well recognized, but it is questionable whether these accumulate sufficiently in the soil under aerobic conditions to affect the reaction appreciably. A more plausible explanation for the increased acidity observed in the soils in this experiment is the accumulation of nitrate nitrogen.

The results of the oxidation-reduction potential determinations are also shown in figure 9, in which it is indicated that the Eh values were lower for the treated soils than for the corresponding untreated soils. The studies reported in the preceding paper (23) on the Eh values at different depths of the same Palouse and Helmer soils under field conditions pointed to definitely and consistently lower values in the upper soil layers, particularly the surface organic layer. Reserves of reducing substances in the organic layer of these soils were presumed to be the cause of the observed lower Eh values. The addition of the surface organic residues of these same soils to the soil samples in this experiment would be expected to produce a drop in the Eh values of these samples, because of the reserves in reducing substances thus incorporated. Evidently such was the case. Another consistent trend indicated in figure 9 is that the Eh values of all the soils, although fluctuating somewhat as did the pH values, increased gradually with time. Heintze (3), and Peech and Batjer (12) noted that high oxidation-reduction potentials of soils are associated with low pH values. The general decrease in the pH values and the coincident increase in Eh values (fig. 9) are in agreement with their observations with respect to the reciprocity of pH and Eh values, but the rising Eh values correspond also with a diminishing supply of organic matter as decomposition proceeded, suggesting a decrease in reserves of reducing substances. It is noticed also that in general the gradual increase in Eh values is more pronounced for the Helmer soils than for the Palouse soils, and for the Helmer-duff-treated Helmer and Palouse soils than for the Palouse-litter-treated Helmer and Palouse soils. These tendencies suggest that the reserve supply of reducing complexes was greater or more active in the Helmer duff and humus. There was no correlation between the observed variations in Eh values and the striking differences in microbial activity in the variously treated soils.

DISCUSSION

The profile characteristics of the Helmer and Palouse soils, vary considerably, though these soils have developed from identical parent material under the same climatic conditions.

Helmer silt loam, a brown colored forest soil, has at the surface a layer of duff ranging from 0.5 to 1.5 inches in thickness. It is underlain by an A_1 horizon, 0.5 to 1.5 inches in thickness and consisting of gray, rather fluffy mineral material mixed with organic matter. The description of Helmer silt loam by Agee, et al. (1) and that of the closely related Santa silt loam by Poulson and Platt (13) do not refer to this layer, which, nevertheless, is present though not everywhere continuous. The underlying A_2 horizon, 6 to 8 inches in thickness, is grayish yellow-brown, somewhat compact, and is underlain by a browner though still grayish mottled and very compact B_1 horizon which extends to a depth of 22 inches. The B_2 horizon, extending from the depth of 22 to between 50 and 60 inches, is slightly less compact, somewhat mottled by clay and sesquioxide illuviation, and is of a tawny yellow-brown color approaching that of the underlying parent material. There is no evidence of calcium carbonate accumulation or of prismatic or columnar structure. In general, the profile characteristics of Helmer silt loam indicate that this soil is closely related to the brown forest soils described by Joffe (7, p. 315–325).

Palouse silt loam, a grassland soil, has relatively little organic residue on its surface. The A_1 horizon, extending to a depth of 4 inches, is brown-black, somewhat laminar, friable, and granular. The A_2 horizon, which is generally about 12 inches thick and is thicker on certain slopes, has a grayish dark brown color and a granular, crumby structure. It is underlain by an 8- to 10-inch layer of light brown compact material of crumby structure, called the A_3 horizon by Poulson and Platt (13). The B horizon extending from the depth of 24 inches to 40 or 50 inches is yellowish-brown compact material showing little tendency to form columns or prisms, although in certain profiles a prismatic structure is evident. The underlying material is free from calcium carbonate, which may be present, however, in certain profiles, depending upon slope and exposure of the land. The profile characteristics of Palouse silt loam used in this investigation indicate that this soil is closely related to the prairie soils.

There is no indication of a former grass type of vegatation on the Helmer soil. If at some time in the past the prairie encroached on the forest, the time is so remote that all traces of an original grassland vegetation have disappeared. The reverse holds true for the Palouse soil.

Vegetation has played a fundamental rôle in differentiating the characteristics of these two soil types, especially those characteristics concerning the amount of humus, the microflora, the soil color, and the soil structure. A consideration of the vegetation is not complete, however, unless both the top growth and the root development receive attention. It is reasonable to suppose that on identical soil materials under the same climatic conditions, at least as much vegetative material, including top and root growth, is produced annually by forest vegetation as by grass vegetation, because the loss of moisture by evaporation is smaller under forest cover than under grass cover. Tree roots withdraw moisture from greater depths in the soil than do grass

roots, and in areas where rainfall is scarce during the summer months, tree vegetation has a longer annual growth period than has grass vegetation. Determinations were made of the annual top growth vegetation on the Palouse soil and of the root material in the surface 10 inches of both the Palouse and the Helmer soils. The results are given in detail in the preceding paper (23), but some of the more pertinent data together with estimates (26, p. 221–226) for the top growth on the Helmer soil are reproduced in table 5, from which the following deductions and comparisons may be made.

The amount of top growth on the Helmer soil (based on estimates) is nearly twice that on the Palouse soil. The amount of root material in the surface 4 inches of the Palouse soil is more than double that in the same layer of the Helmer soil. The difference between the amounts of root material in the 4- to 10-inch layers of the two soils is relatively small. Contrary to the fore-

TABLE 5

Amounts and composition, based on dry weight, of annual top growth and root materials for Palous and Helmer silt loam

SUBSTANCE	HELMER SOIL	HELMER DUFF	HELMER SOIL ROOTS			PALOUSE SOIL	PALOUSE LITTER	PALOUSE SOIL ROOTS		
			Depth, in inches					Depth, in inches		
			0–4	4–10	0–10			0–4	4–10	0–10
Top growth, *tons per acre*	1.37*	.....	....	....	.....	0.71	.....	....	....	.....
Roots, *tons per acre*	....	.....	2.29	2.38	4.67	....	.....	5.16	1.95	7.11
Total C, *per cent*	....	36.69	....	....	48.11	....	32.64	....	....	42.15
Total N, *per cent*	....	0.578	....	....	0.425	....	0.703	....	....	0.585
C:N ratio	....	63.45	....	....	113.20	....	46.39	....	....	72.05
H_2O- and H_2SO_4-soluble C, *per cent*	....	12.46	....	....	13.51	....	18.65	....	....	14.65
H_2SO_4-insoluble C, *per cent*	....	22.78	....	....	26.92	....	12.26	....	....	21.47
H_2O- and H_2SO_4-soluble N, *per cent*	....	0.309	....	....	0.195	....	0.383	....	....	0.351
H_2SO_4-insoluble N, *per cent*	....	0.304	....	....	0.193	....	0.269	....	....	0.194

* Based on average figures from Waksman (26, p. 221–226).

going assumption, that as much vegetative material should be produced on forest as on grassland soils, there is a somewhat greater quantity of top and root material on the Palouse soil than on the Helmer soil. Although not known with certainty, the fine root material in the grassland soils may decompose more rapidly than the relatively coarse roots in the forest soils, and the generation time of the root system may be shorter for grass vegetation than for tree vegetation. These comparisons, though based on tentative data and estimates requiring verification by more extensive investigations, are highly indicative of significant differences in the amounts and types of vegetative materials annually returned to the Palouse and the Helmer soils.

The root material together with the top growth constitutes the major supply of potential organic substance which is eventually transformed to humus under virgin soil conditions. The apparently greater amount of top and root material returned annually to the Palouse soil as compared with that returned

to the Helmer soil and the seemingly more rapid turnover of the grass root system of the former are factors contributing to the difference in humus content in favor of the Palouse soil, but they are not the only factors involved and perhaps not the most influential ones. The composition of the organic residue undoubtedly is another important factor in the transformation of this residue to humus.

It is noted from the data in tables 1 and 5 that the Palouse litter and roots contain more water-soluble and sulfuric-acid-soluble carbon and nitrogen, and less sulfuric-acid-insoluble carbon and nitrogen than do the Helmer duff and roots. The carbon-nitrogen ratios of the Palouse litter and roots respectively are much narrower than those of the Helmer duff and roots. Since the water-soluble and sulfuric-acid-soluble compounds of organic residues decompose much more readily than do the sulfuric-acid-insoluble compounds, as has been pointed out, it might be expected that the top and root materials of the Helmer soil would decompose more slowly than those of the Palouse soil. That such is the case even in the presence of an ample supply of nitrogen was demonstrated in this investigation insofar as decomposition processes can be measured by changes in the carbon compounds. Moreover, the data on CO_2 evolution and total organic carbon in tables 1 and 2 show a greater loss of carbon from soils 4 and 5, the untreated and Palouse-litter-treated Palouse soil respectively, than that from soils 1 and 2, the comparably treated Helmer soils. Yet, the humus content of the Helmer soil proved to be only about two thirds as large as that of the Palouse soil, a difference too large to be fully accounted for by the presumed relatively small difference between the amounts of vegetative residues received annually by these soils. How, then, can this apparent anomaly be explained?

It is significant that the differences in carbon and nitrogen contents of the various extracts obtained from the plant materials of the Palouse and the Helmer soils are not reflected in the same manner in comparable extracts from the humus of these soils. The organic residues (tops and roots) and humus of the Palouse soil contain more water-soluble and sulfuric-acid-soluble carbon and nitrogen than do the same substances of the Helmer soil, but the sulfuric-acid-insoluble carbon and nitrogen, constituting by far the largest percentages of the total carbon and nitrogen and present in much larger percentages in the Helmer duff and roots than in the Palouse litter and roots, occur in similar percentages in the humus of the corresponding soils. The difference between the nature of the humus of the two soils and their corresponding organic residues must be attributed to differences in the process of organic matter transformation, initiated and carried on chiefly by the soil microflora, which is composed predominantly of bacteria and actinomyces in the Palouse soil and of bacteria and fungi in the Helmer soil. Evidently the nature of the humus, disregarding the amount produced from different organic residues, is a function of the particular type of microflora responsible for the decomposition of these residues.

In a consideration of the amount of humus that can be formed per unit of organic material, the carbon-nitrogen ratio of the organic material probably is more important than the type of microflora decomposing the material. Evidence presented in a previous paper (4) leads to the conclusion that under like climatic conditions the aerobic process of transformation of organic residues varying widely in carbon-nitrogen ratios tends to result in the formation of humus with a definite, uniform carbon-nitrogen ratio, indicating that the quantity of humus produced from organic residues is inversely proportional to the carbon-nitrogen ratio of the residues. The carbon-nitrogen ratios of the Helmer duff and roots are much wider than those of the Palouse litter and roots; hence, less humus is formed per unit of vegetative material in the Helmer soil than in the Palouse, provided the carbon-nitrogen ratio in the humus of these soils varies but slightly, as is probable since both soils are formed under the same climatic conditions. The carbon-nitrogen ratios recorded in table 1 are not the ratios for humus, because the carbon values include carbon of live roots and other organic substances in the initial stages of decomposition. The latter, as has been mentioned, are present in greater amounts in the Helmer soil than in the Palouse. Thus, it appears that one of the chief causes of the relatively small percentage of humus in the Helmer soil is the relatively small amount of humus formed per unit of vegetative material. Another probable contributory factor is, as pointed out by Joffe (7, pp. 225–235, 259–261), that grass vegetation contains a larger percentage of ash and bases than does coniferous forest vegetation. The decomposing grass vegetation liberates enough bases to flocculate the organic decomposition products, thereby greatly decreasing their loss by leaching, whereas the decomposing coniferous vegetation liberates an insufficient amount of bases to coagulate the by-products of decomposition, which consequently remain in suspension and suffer loss by leaching to lower horizons.

The aforementioned differences in composition and decomposition of the organic residues result in a relatively efficient humus formation, a comparatively large actinomyces population, a dark color, and a granulated structure in the Palouse soil, in contrast with a less efficient humus formation, a more acid reaction, a comparatively large fungus population, a lighter color, and comparatively little granulation in the Helmer soil. The rôle of the microflora in these processes is very markedly influenced, one might say controlled, by the nature of the organic residues. This was demonstrated by the fact that in the Helmer soil the activity of bacteria and actinomyces was stimulated more and that of the fungi less by Palouse litter and by Helmer duff, and that the effects were in the reverse order in the Palouse soil. If soil material is subjected to different vegetative covers under similar climatic conditions, it may be expected that under forest vegetation, such as covers the Helmer soil, the decomposition of forest organic matter, which is low in bases, will tend to lower the pH value of the medium, and because of the nature of the decomposing organic matter the fungus population, favored from the beginning,

will become further stimulated as the soil develops. Under grass vegetation, such as covers the Palouse soil, the decomposition of the grass organic matter, which is higher in bases, will tend to maintain the pH value of the soil material near the neutral point, and because of the nature of the decomposing organic matter the actinomyces population, large from the beginning, will be increased further as the soil develops. Where the reaction of the two types of soil formed is only slightly acid and varies but little, as in the Palouse and the Helmer soils, the bacteria, though numerous in the soil material from the beginning, will be stimulated more by the organic residues of higher base content than by those of lower base content. The particular type and activity of the soil microflora thus established, chiefly through the nature of the plant residues that are supplied, play an important rôle in the development of specific inherent soil properties during the course of soil formation. Thus, the kind of vegetation and, hence, the quantity and nature of the organic residues added to identical soil materials exposed to similar climatic conditions will result in the production of different amounts of humus and in the development of diverse types of microflora, which, in turn, will produce dissimilar organic decomposition products and types of humus. The influence of these factors is paramount in the differentiation of such inherent soil characteristics as humus content, reaction, color, and structure.

SUMMARY

Virgin Helmer and Palouse silt loams taken from the surface 10 inches were used for microbial and chemical studies of untreated samples of soil, of samples treated with their homologous organic residue, and of samples of one soil treated with the organic residues of the other soil.

The maximum daily CO_2 evolution occurred during the first day and was greater in Palouse soil and Palouse litter than in Helmer soil and Helmer duff, corresponding with the relatively larger amounts of water-soluble and sulfuric-acid-soluble carbon in the humus and surface organic residue of the former soil. There was a lag of 2 or 3 weeks between maximum CO_2 production and maximum numbers of microbes, indicating that CO_2 production was by no means an accurate index of microbial numbers.

The Helmer soils supported larger numbers of fungi and bacteria, and smaller numbers of actinomyces than did the corresponding Palouse soils. In the Helmer soils the fungi were stimulated more, and the bacteria and especially the actinomyces less, by the addition of Helmer duff than by the addition of Palouse litter. In the Palouse soils the actinomyces were stimulated much more, and the bacteria and fungi less by the addition of Palouse litter than by the addition of Helmer duff.

The aerobic cellulose-decomposing bacteria although few in number were stimulated markedly in both soils by the addition of organic residues. No *Azotobacter* and only small numbers of anaerobic nitrogen-fixing bacteria were found in these soils, irrespective of treatment.

In the process of decomposition of the organic residues the fungi reached maximum numbers first, followed closely by the bacteria, later by the actinomyces, and finally by the aerobic cellulose-decomposing bacteria. The bacteria and fungi appeared to be chiefly responsible for the decomposition processes in the Helmer soils, and the bacteria and actinomyces for these processes in the Palouse soils.

The water-soluble carbon and nitrogen decomposed very rapidly, particularly during the time when the bacteria and fungi were most active. The sulfuric-acid-soluble carbon and nitrogen proved to be more resistant to decomposition, but the loss was greatest in the soils with the largest numbers of actinomyces, suggesting that these substances constitute a more suitable food for actinomyces than for bacteria and fungi. The decrease in sulfuric-acid-insoluble carbon was very small, and a slight gain in sulfuric-acid-insoluble nitrogen was realized in certain soils, probably because of protein synthesis by the microflora.

The roots and surface organic residue of the Palouse soil contained more water-soluble and sulfuric-acid-soluble carbon and nitrogen and less sulfuric-acid-insoluble carbon and nitrogen than did the corresponding substances of the Helmer soil, whereas the humus in the Palouse soil, as compared with that in the Helmer soil, contained not only more water-soluble and sulfuric-acid-soluble carbon and nitrogen but also similar percentages of sulfuric-acid-insoluble carbon and nitrogen. The latter were attributed to differences in type and activity of the microflora.

A small but consistent loss of nitrogen from all the soils was observed. Larger amounts of nitrate nitrogen accumulated in the Palouse soils than in the similarly treated Helmer soils. The ammonia nitrogen content of the soils decreased rapidly as their nitrate nitrogen content increased, and this was associated with a gradual reduction in pH values. The oxidation-reduction potentials were lower in the treated soils than in the untreated soils and increased in all soils with the decrease in pH values and organic matter.

The influence of vegetation on the type and activity of the microflora that is likely to prevail, and the nature of humus and inherent soil characteristics that may result in soils developed from identical parent materials under similar climatic conditions are discussed.

REFERENCES

(1) Agee, J. H., Graves, G. W., and Mickelwaite, C. B. 1915 Soil Survey of Latah County, Idaho. Advance Sheets, Field Operations, Bur. Soils, U. S. Dept. Agr. 1–24.

(2) Cobb, M. J. 1932 A quantitative study of the microörganic population of a hemlock and a deciduous forest soil. *Soil Sci.* 33: 325–345.

(3) Heintze, S. G. 1934 Use of the glass electrode in soil reaction and oxidation-reduction potentials of soils. *Jour. Agr. Sci.* 24: 28–41.

(4) Holtz, H. F., and Vandecaveye, S. C. 1938 Organic residues and nitrogen fertilizers in relation to the productivity and humus content of Palouse silt loam. *Soil Sci.* 45: 143–163.

(5) HUTCHINGS, I. J., AND MARTIN, T. L. 1934 Influence of the C:N ratios of organic matter on the rate of decomposition in the soil. *Jour. Amer. Soc. Agron.* 26: 333–341.

(6) JENSEN, H. L. 1935 Contribution to the microbiology of Australian soils: III. The Rossi-Cholodny method as a quantitative index of the growth of fungi in the soil, with some preliminary observations on the influence of organic matter on the soil microflora. *Proc. Linn. Soc. N. S. Wales* 60: 145–154.

(7) JOFFE, J. S. 1936 Pedology. Rutgers Univ. Press, New Brunswick, N. J.

(8) JOHANNSON, N. 1929 Rhythmische Schwankungen in der Aktivitat der Mikroorganismen des Bodens. *Svensk Bot. Tidskr.* 23: 241–260.

(9) ITANO, A., AND ARAKAWA, S. 1931 Microbiology of organic matter: I. Microbiological decomposition of rape cake in soils under the puddy-field and dry-farm conditions. *Jour. Sci. Soil Manure (Japan)* 5: 12–21.

(10) MELIN, E. 1930 Biological decomposition of some types of litter from North American forests. *Ecology* 11: 72–101.

(11) NORMAN, A. G. 1931 The biological decomposition of plant materials: IV. The biochemical activities in straw of some cellulose decomposing fungi. *Ann. Appl. Biol.* 18: 244–259.

(12) PEECH, M., AND BATJER, L. P. 1935 A critical study of the methods for measuring oxidation-reduction potentials of soils with special reference to orchard soils. *N. Y. (Cornell) Agr. Exp. Sta. Bul.* 625: 1–23.

(13) POULSON, E. N., AND PLATT, K. B. 1930 Soil survey of Benewah County, Idaho. *Bur. Chem. and Soils, U. S. Dept. Agr.* 22: 1–34.

(14) POWERS, W. L., AND BOLLEN, W. B. 1934 Forest fertility studies. *Amer. Soil Survey Assoc. Bul.* 15: 24.

(15) ROMELL, L. G. 1932 Mull and duff as biotic equilibria. *Soil Sci.* 34: 161–188.

(16) SMITH, F. B., BROWN, P. E., AND MILLAR, H. C. 1935 The rhythmical nature of microbiological activity in soil as indicated by the evolution of carbon dioxide. *Jour. Amer. Soc. Agron.* 27: 104–108.

(17) STARKEY, R. L. 1924 Some observations on the decomposition of organic matter in the soil. *Soil Sci.* 17: 293–314.

(18) STEPHENSON, R. E. 1936 The nitrification process and plant nutrition. *Soil Sci.* 41: 187–197.

(19) STURGIS, M. M. 1932 Determination of the rate of decomposition of organic matter under field conditions. *Soil Sci.* 34: 19–23.

(20) TENNEY, F. G., AND WAKSMAN, S. A. 1929 Composition of natural organic materials and their decomposition in the soil: IV. Nature and rapidity of decomposition of various organic complexes in different plant materials under aerobic conditions. *Soil Sci.* 28: 55–85.

(21) VANDECAVEYE, S. C., AND ALLEN, M. C. 1935 Microbial activities in soil: II. Activity of specific groups of microbes in relation to organic matter transformation in Palouse silt loam. *Soil Sci.* 40: 331–343.

(22) VANDECAVEYE, S. C., AND BAKER, G. O. 1938 Microbial activities in soil: III. Activity of specific groups of microbes in different soils. *Soil Sci.* 45: 315–333.

(23) VANDECAVEYE, S. C., AND KATZNELSON, H. 1938 Microbial activities in soil: IV. Microflora of different zonal soil types developed under similar climatic conditions. *Soil Sci.* 46: 57–74.

(24) WAKSMAN, S. A. 1924 Influence of microörganisms upon the C:N ratio in the soil. *Jour. Agr. Res.* 14: 555–562.

(25) WAKSMAN, S. A. 1926 Origin and nature of soil organic matter or soil "humus": V. The rôle of microörganisms in the formation of "humus" in the soil. *Soil Sci.* 22: 421–436.

(26) WAKSMAN, S. A. 1936 Humus. Williams and Wilkins Co., Baltimore, Md.

(27) WAKSMAN, S. A., AND HUTCHINGS, I. J. 1935 Chemical nature of organic matter in different soil types. *Soil Sci.* 40: 347–363.

(28) WAKSMAN, S. A., AND STARKEY, R. L. 1931 The Soil and the Microbe. John Wiley & Sons, Inc., New York.

(29) WAKSMAN, S. A., AND STEVENS, K. R. 1930 A system of proximate chemical analysis of plant materials. *Indus. and Engin. Chem.* 2: 167.

(30) WAKSMAN, S. A., AND TENNEY, F. G. 1927, 1928 Composition of natural organic materials and their decomposition in the soil: II. *Soil Sci.* 24: 317–333 (1927); III. 26: 155–171 (1928).

(31) WAKSMAN, S. A., TENNEY, F. G., AND STEVENS, K. R. 1928 Rôle of microörganisms in the transformation of organic matter in forest soils. *Ecology* 9: 126–144.

(32) WATSON, C. W. 1932 Changes in composition of organic matter in the process of formation of humus horizons from forest liter. *Amer. Soil Survey Assoc. Bul.* 13: 15–20.

BOOK REVIEWS

Principles of Feeding Farm Animals. Revised Edition. By SLEETER BULL AND W. E. CARROLL. The Macmillian Company, New York, 1937. Pp. xi + 395, figs. 60, tables 22. Price $2.90.

Studies carried out by the Federal Department of Agriculture in 1922–23 showed that approximately three quarters of the product of crop land is used for the feeding of farm animals. This is aside from our humid pastures and the arid and semiarid grazing lands. It has been pointed out by a number of investigators that the mechanization of our farms has led to the elimination of horses and mules equivalent to the produce of 25 to 40 millions of acres. At the same time, it is widely recognized that the efficiency of our meat and dairy animals has been very substantially increased in respect to the utilization of animal foods. Altogether, we are dealing with an economic factor of wide significance.

The present volume is a timely contribution to the subject. It will be of more direct value to the students in our vocational schools and our colleges, and, likewise, to livestock producers, than to the more advanced students of animal nutrition. This fact is noted by the authors in the preface to their book, as follows: "An effort has been made to present the scientific facts underlying the art of feeding animals in such a manner that the book will not only be suitable for use as a text for elementary courses in general feeding, but will also be valuable to the farmer who has not had a technical education in agriculture. Thus it has been deemed wise to omit many minor details and a large part of the mass of experimental data from which the general conclusions are deduced."

Principles of Feeding Farm Animals contains 21 chapters, an appendix, and an index. The titles of the several chapters follow: The Chemical Composition of Feedingstuffs; The Chemical Composition of Farm Animals; The Digestion of the Nutrients; The Digestibility of Feedingstuffs; Functions of the Feed Nutrients in the Animal Body; Energy in Feedingstuffs and its Uses in the Animal Body; The Compounding of Rations; The Feed Requirements of Farm Animals; Grains and Seeds; The Cereal By-Products; The Oil By-Products; The Packinghouse By-Products; Miscellaneous Concentrates; The Hays; Fodders and Stovers; The Straws; Pasture Crops; Silage; Miscellaneous Roughages; Factors Affecting the Utilization of Rations; and The Fertilizing Values of Feedingstuffs.

The Flow of Homogeneous Fluids Through Porous Media. By M. MUSKAT. McGraw-Hill Book Company, New York and London, 1937. Pp. xix 763, figs. 284. Price $8.

To say the least, this book represents a very ambitious undertaking. Its method of approach opens broad vistas on major physical and economic questions. The scope of the work is well indicated in the introduction, prepared by R. D. Wyckoff. He says:

> The subject matter of this treatise, the flow of homogeneous fluids through porous media, while distinctly limited by the qualifications "homogeneous" and "porous," is nevertheless sufficiently wide in scope to find application in many branches of applied science. In such fields as ground-water hydrology, encompassing the provision and maintenance of water supplies, irrigation, and drainage problems, and petroleum engineering, involving the production of gas and oil from their underground reservoirs, the applications are evidently of basic importance. Equally important are applications to specific problems encountered in civil engineering, agricultural engineering, and many industries. Thus the diffusion and flow of fluids through ceramic materials as bricks and porous earthenware has long been a problem in the ceramic industry, and the flow of gas through molding sand a problem of the foundry. The construction of filter beds for municipal water systems and the question of water seepage through, around, and beneath dams, earthen reservoirs, and the like, have been important phases of civil engineering for which satisfactory discussions have been available only within the last few years. The scientific treatment of the problems of irrigation, soil erosion, and tile drainage, although still open to further development, can be considered already as a well-established branch of the general theory of the flow of fluids through porous media. The draining of artesian basins by deep wells or of rivers and canals by wells contiguous thereto is a problem in the flow of liquids through porous rocks or sands, as is the general subject of ground-water hydrology. And, of course, the whole physical problem of the production of oil and gas from underground sources is nothing more than that of fluid flow through porous media.

The book is made up of a preface, four parts, six appendixes, and author and subject indexes. The four parts deal, respectively, with: Foundations; Steady-State Flow of Liquids; The Nonsteady-State Flow of Liquids; and The Flow of Gases Through Porous Media. There are, in all, eleven chapters in the book, which are made up of numerous subdivisions.

The author is to be commended for having produced a scholarly treatise of far-reaching significance. Geologists, engineers, economists, manufactures, and business executives will—directly or indirectly—derive benefit from this work. It should find a place on the reference shelf of every modern library.

Parkways and Land Values. By JOHN NOLEN AND HENRY V. HUBBARD. Harvard University Press, Cambridge, Mass., 1937. Pp. xiv + 135, figs. 23, plates 11, tables 12. Price $1.50.

The preface, prepared by Henry Vincent Hubbard, indicates the thoughts that guided the authors in the preparation of this book. The following may be quoted:

> In 1930 Mr. John Nolen and I, in the course of one of our very many discussions of planning matters, found ourselves particularly interested in the changing functions of the parkway in the regional plan, and in the wide differences which we knew to exist in its nomenclature, in evaluation of its service, and in expectation of its future benefits under modern circum-

stances. We felt that it would be well worth the effort to attempt to clarify our own thinking in these matters and to put our results at the disposal of others whose thoughts like ours needed some crystallization. We had no desire to prove one thing rather than another. We were concerned only to set down what the facts were and what conclusions, whether we liked them or not, seemed to us more or less inevitable from the facts.

The book contains five chapters, designated respectively: Possibilities or Evaluation of Benefits and Allocation of Costs; Parkways of Metropolitan Boston; Kansas City Parkways; Westchester County Parkways; and Summary and General Remarks. There are likewise two appendixes, entitled: List of More Important References; and Organizations and Persons Coöperating with the Harvard Department of Regional Planning on the Parkway Study.

The major emphasis that is now being laid on the providing of adequate recreation facilities is in keeping with some of the important trends noted by the authors. The Regional Plan Association in the New York metropolitan area has taken cognizance of some of the more significant problems involved in regional and national planning. It has been pointed out time and again by our leading planners that there should be ten acres of recreation areas for every one thousand persons living in our cities. This is aside from municipal, state, and national forests. The subject dealt with by the authors cannot be divorced from city planning, water supplies, sewage disposal, and land use in general. The broad subject of land-use planning must, of necessity, reckon with parkways and land values. This book, undoubtedly, will prove helpful to all interested in improving transportation and recreation facilities and in the betterment of esthetic and social conditions.

Practical Methods in Biochemistry. Second Edition. By FREDERICK C. KOCH. William Wood & Company, Baltimore, 1938. Pp. viii + 302, tables 29. Price $2.25.

The first edition of this book appeared in 1934. It was reprinted in August, 1935, and a second edition appeared in September, 1937. It is noted by the author in the preface to the second edition that "In this revision I have eliminated some of the duplications of methods, have revised others and have added specific instructions on urea clearance and on the quantitative estimation of albumin, globulin, sodium and potassium in blood serum."

The book is made up of three parts, entitled respectively: The Chemistry of Cell Constituents; The Chemistry of the Digestive Tract; and Blood and Urine. There are 13 chapters, designated as follows: Carbohydrates; Lipins; Proteins; Nucleoproteins and Nucleic Acids; Hydrogen Ion Concentration; Salivary Digestion; Gastric Digestion; Intestinal Digestion; Bile; Blood and Hemoglobin; The Quantitative Analysis of Blood; The Quantitative Analysis of Urine; and The Chemical Examination of Urine for Pathological Conditions. There are also an appendix, alphabetical list of reagents and amounts needed per student, and an index.

It was pointed out in the preface to the first edition that the author had in

mind a manual that would be helpful to medical students. The information that had been compiled, arranged, and interpreted by the author will prove useful, however, to many other than medical students. It has distinct value as a reference as well as a text book.

Man, Bread and Destiny. By C. C. FURNAS AND S. M. FURNAS. The Williams & Wilkins Company, Baltimore, 1937. Pp. xix + 364. Price $3.

The authors must have felt some satisfaction in the inscription which they offer, namely: "To our respective fathers who might still be alive if nutritional knowledge had been complete during their lifetimes." Perhaps this is more than a pious wish. Be it as it may, many persons have died before their time because they did not eat enough, or because they ate too much, or because they ate the wrong things.

No one will quarrel with the authors because they have entitled their introductory statement "A Man Must Eat." In fact, most men and women—to say nothing of children—like to eat. Science and technology have helped us to produce more and better food, and have, likewise, pointed out to us the pitfalls of malnutrition.

The contents of the book are divided into seven parts and a total of 20 chapters. These are followed by an appendix, notes, and an index. The several parts and chapters are designated as follows: Part One—Historical: The Savage Brute, and Early Ramblings in Nutrition; Part Two—The Power House: Energy, and Quantity; Part Three—Essential Fuel: The Big Three, Minerals, and Vitamins; Part Four—Good Food—Good Health: Jackstraws, Decaying Teeth Through the Ages, Diet and Mentality, Stamina, and Gullible's Travels; Part Five—Come and Get It: On Dining Well, Going Through the Mill, Germs vs. Eating, What Cooks Forget, and Cook Book Review; Part Six—Economic Aspects: The Eating World, and Filling the Pantry; Part Seven—The Future of Food: Helping Nature.

By the designation used, the authors make it clear to the reader that the book is intended to make a strong popular appeal. They have succeeded in showing that food is a source of energy—raw material for the building of animal tissues and a vital part of our whole political, economic, and social structure. Teachers, dieticians, home demonstration agents, and well-informed men and women, in general, will find in this book concrete information and helpful suggestions.

Mother Earth. By GILBERT WOODING ROBINSON. Thomas Murby & Co., London, 1937. Pp. viii + 202, maps 2, figs. 6, plates 1. Price 5/6 net.

This little book is full of stimulating thought. The author has tried to grasp the fundamental relations and significance of land-use factors in the unfolding of human history. As populations grow or decline, as individuals and groups move from region to region, land and soil factors somehow make

themselves felt. In this connection, the statement addressed to the general reader by the author may be quoted:

I have addressed these Letters on Soil to an old friend and colleague who is probably better known to the public than I am. Although he may not agree with all that has been written herein, I know he will read them with attention, because they are about the Soil, which is the Land. And because so many have read what he has written about the land, I dare to hope that some may read these letters with interest, for they deal with matters on which we ought to think rightly. The affairs of the soil may not have the strange magnificence of the outer universe or the curiosity of the inner recesses of the moon; but they touch our daily lives more intimately. So I commend them to your notice and ask your indulgence for the homeliness of my story.

We may also note the following quotation from St. Francis of Assisi:

Praised be, my Lord, for our sister, Mother Earth, which doth sustain and keep us, and bringest forth divers fruits, and flowers of many colours, and grass.

The book contains 17 chapters, designated as follows: Introductory; Soil or A Soil; Soil Material; Humus; Structure and Tilth; The Soil Profile; Some Typical Soils; Soil Moisture; Soil Fertility; Manures and Fertilizers; Lime; Soil Surveys; Arable, Grass and Forest; Our Agricultural Soils; Waste Lands; Corruptio Optimi Pessima; and Concluding Reflections.

Finally, we may note the concluding paragraph by Doctor Robinson. It may have been written from the point of view of the British Isles. None the less, the statement has very general application:

Viewing the future of the soils of the world and realizing that their resources for food production are more limited than was formerly supposed, I cannot avoid the conclusion that our own soil must bear a larger share in the provision of our food. The present campaign for raising the level of fertility of our soil has originated under the threat of war. It is no less necessary if we remain at peace. I believe that the solution of the problem will be found, not in the adoption of revolutionary and artificial methods, but in the enlightened yet conservative use of our natural resources of soil and climate, with Science always the servant but never the master.

Theory and Practice in the Use of Fertilizers. Second Edition. By FIRMAN E. BEAR. John Wiley & Sons, Inc., New York, 1938. Pp. ix + 360, figs. 63, tables 71.

The first edition of this book appeared in 1929. It found ready use in many classrooms. The second edition brings up to date some of the newer trends and developments in the field of fertilizer manufacture and practice. In the preface to the second edition, the author notes:

Progress in the manufacture and use of fertilizers has been very rapid during the period that has elapsed since the first edition of this book was published. Accordingly, it became necessary to make a number of changes throughout the text, to rewrite several chapters entirely, and to add a chapter on "trace" elements. It is hoped that, with these changes, the book may continue to serve a useful purpose to those interested in the growing of higher acre yields of the standard crops.

The 20 chapters and the index which make up the book do not, generally speaking, differ greatly from the make-up of the first edition. As the author points out, however, the second edition contains one more chapter than the first edition. This has to do with *trace* elements in soils and crops.

The student of soils, the agronomist, and the progressive farmer may depend on this book for factual information developed by the American experiment stations. Fertilizer materials have changed in character, as has soil management from the point of view of fertilizer practice. Among the newer developments in the manufacture and use of commercial fertilizers, mention may be made of fertilizer placement experiments and the addition to mixed fertilizers of small quantities of so-called *trace* elements. Altogether, the newer processes of fertilizer manufacture, the newer types of fertilizer materials on the market, and the newer methods of applying fertilizer are all widely understood. The author takes cognizance of all of these changes in the manufacture and use of commercial fertilizers.

Knowing Your Trees. By C. H. COLLINGWOOD. The American Forestry Association, Washngton, D. C., 1937. Pp. 109, illus. 246.

The American Forestry Association, under whose auspices this book was published, has placed under debt to itself a great number of intelligent and public-spirited persons. It has helped to visualize the meaning of trees and forests in our national economy.

This volume contains a foreword, 50 chapters dealing with individual species and varieties of trees, and an index.

The why of this book is indicated in the foreword. The following may be quoted:

> This book—"Knowing your Trees,"—is a response to this public demand for the first fifty tree descriptions which have appeared in American Forests, with all statistical data brought up to the latest available figures. Similar descriptions of other native or adopted trees will continue to appear in the magazine from month to month until all trees familiar to the American landscape have been presented. From time to time these will also be assembled in book form.

Aside from the helpful information contained in the text, the numerous and fine illustrations should receive special commendation. Both the student and the general reader will find much satisfaction in adding this book to their reference shelves.

JACOB G. LIPMAN